Fabrication and Property Evaluation of a Epoxy-Clay-PET Nanocomposite System

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Madhav Raturi
Regd. No. 801282010

Under the guidance of

Dr. Tarun Nanda	**Dr. Rajeev Mehta**
Assistant Professor	Professor
MED, TU, Patiala	CED, TU, Patiala

to the

MECHANICAL ENGINEERING DEPARTMENT

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Certificate

I hereby declare that the thesis entitled **"Fabrication and Property Evaluation of a Epoxy-Clay-PET Nanocomposite System"** is an authentic record of my study carried out as requirements for the award of the degree of Master of Engineering in Production Engineering at Thapar University, Patiala under the supervision of **Dr. Tarun Nanda**, Assistant Professor, Mechanical Engineering Department, Thapar University, Patiala and **Dr. Rajeev Mehta Associate Professor**, Chemical Engineering Department, Thapar University, Patiala during July, 2012 Year to July, 2014Year. The matter embodied in this report has not been submitted in partial or full to any other university or institute for the award of any degree.

Place: Patiala
Date: 21/7/2014

Madhav Raturi

It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

Dr. Tarun Nanda
Assitant Professor
Mechanical Engineering Department
Thapar University, Patiala - 147004

Dr. Rajeev Mehta
Professor
Chemical Engineering Department
Thapar University, Patiala - 147004

Countersigned by

Dr. Ajay Batish
Professor and Head
Mechanical Engineering Department
Thapar University, Patiala - 147004

Dr. S.K. Mohapatra
Dean of Academic Affairs
Thapar University, Patiala - 147004

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Abstract

Nanocomposites are reported to be the materials of 21st century in the view of their unusual properties and unique design possibilities that are not exhibited by conventional composites.

The objective of this work is to gain insight with regards to properties of nanocomposites mainly comprising of Polyethylene terephthalate (PET) as fiber, montmorillonite (MMT) clay as nano-filler and Epoxy as the matrix.

Nano–particles and nano–layers have very high surface–to–volume and aspect ratios and this makes them ideal for use in polymeric materials. Such structures combine the best properties of each component to possess enhanced mechanical and superconducting properties for advanced applications. The physical, chemical and biological properties of nano materials differ from the properties of individual atoms and molecules or bulk matter. By creating nano particles, it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity and even their color without changing the materials chemical compositions.

The present work describes the fabrication, characterization and subsequent mechanical testing of a nanocomposite system containing both nano (clay) and micro (PET fibers) fillers. The experimental work describes the sequence of processing steps required to prepare nanocomposites. The study evaluates the effect of change in filler concentration on the tensile strength, bending strength and flexural modulus of nanocomposites. The study also describes the surface modification procedure for PET fibers to achieve enhanced interfacial bonding between these micro fillers and the epoxy matrix. Fibers have been treated in an alkaline solution of fixed concentration subjected to different treatment time and temperature conditions. The work also compares the properties of the nanocomposites with the treated fibers under the selected treatment conditions with those with untreated fibers.

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List of Acronyms

Acronym	**Full Name**
AC	Alternating Current
ASTM	American Society for Testing and Materials
BMC	Bulk Molding Compound
CDT	Corona Discharge Treated
CMC	Ceramic Matrix Composite
DC	Direct Current
DGEBA	Diglycidyl Ether of Bisphenol A
DMT	Dimethyl Terephthalate
DMT	Dimethyltryptamine
DOE	Design of Experiment
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-Ray
EG	Ethylene Glycol
FRP	Fiber Reinforced Polymers
FRP	Fibre-reinforced plastic
ILSS	Inter-Laminar Shear Strength
IS	Impact Strength
LM	Layered Manufacturing
MMC	Metal Matrix Composite
MMT	Montmorillonite
OMMT	Organo-Montmorillonite
PET	Poly Ethylene Terephthalate
PMDC	Permanent Magnet Direct Current Motors
PMNC	Polymer Matrix Nanocomposites
PP	Polypropylene
PVR	Poly Vinylpyr-Rolidone
RPETFS	Recycled Poly Ethylene Terephthalate Fibers
SEM	Scanning Electron Microscope
SMC	Sheet Molding Compound
SS	Sum of Squares

TEM	Transmission Electrone Microscope
TGA	Thermo-Gravimetric Analysis
THF	Tetrahydrofuran
TOF-SIMS	Time Of Flight Secondary Ion Mass Spectrometry
TPU	Thermoplastic Polyurethane
TS	Tensile Strength
UTM	Universal Testing Machine
UV	Ultraviolet
WAXD	Wide Angle X-Ray Diffraction
XRD	X-Ray Differaction

Symbols

Symbol	**Full Name**
θ	Theta
ϕ	Phi
Å	Angstrom
≈	Almost equal to

Chapter 1

Introduction

1.1 Introduction

A composite material is a material system composed of a suitably arranged mixture or combination of two or more nano, micro, or macro constituents with an interface separating them that differ in form and chemical composition and are essentially insoluble in each other (Smith and Hashemi, 2008). A composite, in the present context, is a multiphase material that is artificially made, as opposed to one that occurs or forms naturally. The constituent phases must be chemically dissimilar and separated by a distinct interface. A composite is considered to be any multiphase material that exhibits significant properties of both constituent phases such that a better combination of properties is realized (Callister, 2007). Composites materials comprise of three main functional constituents:

- Matrix (primary phase)
- Reinforcement (secondary phase)
- Interface

The matrix (or primary phase) binds the fibers together freezing in the fiber orientation, if any. Loads applied to the composite are then transferred into the fibers, the principal load–bearing component, through the matrix, enabling the composite to withstand compression, flexural and shear forces as well as tensile loads. The ability of composites reinforced with short fibers to support loads of any kind is dependent on the presence of the matrix as the load–transfer medium, and the efficiency of this load transfer is directly related to the quality of the fiber/matrix interfacial bond. The matrix must isolate the fibers from each other so that they can act as separate entities. The matrix should also protect the reinforcing filaments from mechanical damage (e.g. abrasion etc.) and from environmental attack. For example, for composites like MMCs or CMCs operating at elevated temperature, the matrix needs to protect the fibers from oxidative attack (Harris, 1999).

The reinforcement is the major load–bearing component in any composite. The reinforcement (secondary phase or dispersed phase) may be of nano, micro, or macro level. The different sizes of reinforcements help in the strengthening of composite by different mechanisms. Generally reinforcement is stiffer or harder in nature than the matrix. The degree of reinforcement or improvement of mechanical behavior depends on strong bonding at the matrix and reinforcement interface (Smith and Hashemi, 2008).

In materials where the mechanical response depends on loads being shared between two or more separate constituents or phases and where paths for the propagation of cracks will be affected by the different mechanical properties of the components, the manner in which these adhere to each other becomes an important consideration. When the strength and toughness of composites is discussed, the strength of the interfacial bond between the fibers and the matrix becomes of great importance. Initially, it was assumed that higher was the fiber stiffness, poorer was the extent to which the composite was able to resist shear forces acting in the plane of a laminate. Interface properties depend upon the chemical and physical nature of the fibers and the matrix; there will be some modification of either chemical or physical characteristics, or both, resulting in a region which has properties quite different from those of either of the two major components. Whatever may be the origin of this region (referred to as the ‘interface’), it is the interface’s properties which determine the manner in which stresses are transferred from matrix to fibers and, in consequence, decide many of the chemical, physical and mechanical properties of the composite (Harris, 1999).

1.2 Nanocomposites

The nanocomposite material is an innovative product having nano (one–billionth of a meter) fillers dispersed in the matrix. Typically, the structure is a matrix–filler combination where the fillers like particles, fibers, or fragments surrounds and binds together as discrete units in the matrix. *Nanocomposites are also described as multiphase composite materials where one of the phases has one, two or three dimensions of less than 100 nano-meter or structures having nano-scale repeat distances between the different phases that make up the material.*

1.2.1 Significance of Nanocomposites

Nano–particles and nano–layers have very high surface–to–volume and aspect ratios and this makes them ideal for use in polymeric materials. Such structures combine the best properties of each component to possess enhanced mechanical and superconducting properties for advanced applications. The physical, chemical and biological properties of nano materials differ from the properties of individual atoms and molecules or bulk matter. By creating nano particles, it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity and even their color without changing the materials chemical compositions.

Recent advances in producing nano–structured materials with novel properties have stimulated research to create multifunctional engineering materials by designing structures at nanometer scale. In this context, the usage of nano/ micro–scale fillers in polymers and fiber reinforced composites has attracted considerable interest. Such fillers frequently exhibit larger surface area per unit volume and thus enhance the performance of the fabricated composite (Hamidi *et al.*, 2008). At nano level, some compounds transform from inert to active, from electrical insulator to conductors, from fragile to tough. They become stronger, lighter and more resistant. These transformed properties are what account for the infinite potential applications of nano–materials. Nano–composites have gained much interest recently. Significant efforts are underway to control the nano–structures via innovative synthetic approaches. The properties of nano–composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. By optimized fabrication process and controlled nano–sized second phase dispersion, thermal stability and mechanical properties such as adhesion resistance, flexural strength, toughness and hardness can be enhanced.

1.3 Polymer Matrix Nanocomposites (PMNCs)

Most commonly used matrix materials in composites are polymeric. The reasons for this are twofold. In general, the mechanical properties of polymers are inadequate for many structural purposes. In particular, their strength and stiffness are low compared to metals and ceramics. These difficulties are overcome by reinforcing other materials with polymers. Secondly, the processing of polymer matrix composites need not involve high pressures and temperatures. Also, the equipments required for manufacturing polymer matrix composites are simpler. For this reason, polymer matrix composites are finding use in numerous structural applications.

PMNCs are polymers (thermoplastics, thermosets, and elastomers) that have been reinforced with small quantities of nano–sized fillers. These are emerging as a new class of industrially important materials with significantly enhanced mechanical and barrier properties, flame retardancy, and electrical conductivity. At loading levels of 2–3 wt. %, they offer similar performance as that of conventional polymeric composites with 30–50 wt. % of reinforcing material (Utracki, 2004).

1.4 Composition of the Proposed Nanocomposite

The nanocomposite fabrication proposed in the present study consolidates it around three major constituents are as follows:

1.4.1 Epoxy Resin (Matrix)

Epoxy is preferred as a matrix over polyesters and vinyl esters because of some of its unique properties. Epoxy is compatible with wide a range of fibers and fillers. Polyesters and vinyl esters are prone to water degradation due to the presence of hydrolysable ester groups whereas epoxy has high resistance to water degradation hence; it is more suitable for marine applications. Adhesive properties of epoxy due its polar hydroxyl and ether groups; and due to its low shrinkage after cure is another advantage because it regulates the strength of interface, which is the weakest point of any composite. Epoxy resins based polymer matrix nano–composites (PMNCs) show excellent chemical resistance and are simple in processing. Due to low density (of around 1.3 g/cm^3) along with good adhesive and mechanical properties, epoxy resin has become a promising material for many high performance applications.

1.4.2 Poly ethylene terephthalate Fiber (Reinforcement)

Poly ethylene terephthalate (PET) belonging to thermoplastic polymers are thermally stable and their properties do not deteriorate upon exposure to moisture. Also, the ductile nature of PET imparts toughness to the matrix. It is one of the most important fibers for industrial production due its high strength, low cost, and recyclability. The present work proposes to use

PET fiber as reinforcement in epoxy based nanocomposites because of its following characteristics:

- **High availability of recycled PET (Eco–Friendly):** Today, the largest use of PET is in containers with maximum usage in beverage bottles. In 1995, 1.2 million tons of containers of PET were recycled (Santos and Pezzin, 2003). The interest in recycled materials developed from post–consumer polymers has been gaining a lot of attention due to serious environmental hazards (Favaro *et al*., 2010). As a result, recycling of polymers is receiving attention by the researchers and the proposed work is a step in that direction.
- **Low density:** PET has a low density in the range of 1.3–1.4 g/cm^3. The composite obtained with PET reinforcement will be light in weight, which makes it appropriate for many applications viz. aerospace industry.
- **Improved Barrier Properties:** The incorporation of plate–like fillers with a high aspect ratio is found to improve the barrier properties of composites towards low molecular weight compounds viz. O_2, CO_2, water vapors etc.(Kotsilkova, 2007). The use of PET fibers in epoxy based nanocomposites with organically modified nano–clay creates tortuous pathways for the passage of fluids, thus decreasing permeability.
- **Cost Effectiveness:** PET can be a very low cost alternative to other commonly used fillers such as aramid, glass fibers, carbon nanotubes etc.
- **Improved Interfacial Bonding:** PET fibers respond positively to simple surface treatments (alkaline treatment with NaOH, ultraviolet treatment, plasma treatment etc.) for their surface modification and provide improved interfacial adhesion of the reinforcement with the polymer matrix. Surface treatments (e.g. NaOH treatment) are very cost–effective, which do not require any additional/ sophisticated/costly equipments but results in improved mechanical properties.

1.4.3 MMT Clay (Montmorillonite)

Among the different type of clay minerals, MMT is the most commonly used for the preparation of polymer clay nanocomposites. MMT owes special attention among its group due to its ability to show extensive inter layer expansion or swelling because of its peculiar structure. The silicate layers of MMT are planar, stiff about 1 nm in thickness with high aspect ratio and large active surface area. These layers organize themselves in a parallel way to form stacks with a regular van der Walls gap in between them, called as interlayer or gallery (Azeez *et al.*, 2013).

Generally clays are hydrophilic in nature. In order to make them compatible with organic polymers, the surface of the clay minerals should be modified to organophilic prior to its use. Organic cations such as an ammonium ion or phosphonium ion are commonly used organic modifiers for clay minerals. Modification involves the exchange of interlayer inorganic cations with organic onium salts. The organic modification causes the expansion of the interlayer space and thereby increases the d–spacing to certain extent (normally over 2 nm). Thus the organic modification favors the diffusion of polymer or its precursor into the interlayer space. Figure 1.1 shows the schematic representation of the organic modification of clay (Azeez *et al.*, 2013).

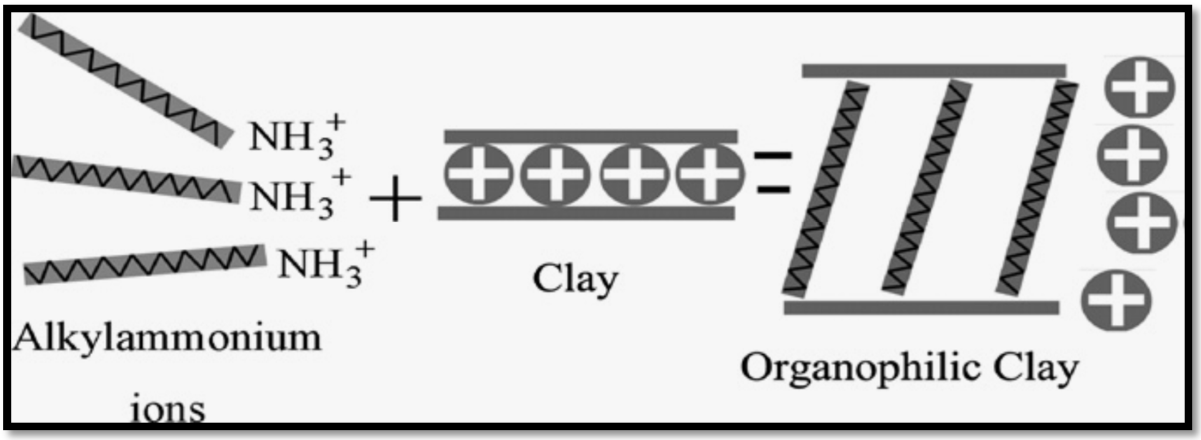


Fig. 1.1 Organic modification of clay (Image Source: Azeez *et al.*, 2013)

Montmorillonite can be employed in the preparation of polymer–clay nanocomposites because of its typical performance advantages, compared to other traditional reinforcing agents. The advantages include:

- ❖ Montmorillonite develops similar increase in modulus and tensile strength at 3–5% loading compared to 20–60% loading of conventional reinforcing agents such as kaolin, silica, talc, and carbon black. Implicit advantages include lighter plastic parts with greater transparency.
- ❖ Montmorillonite increases barrier properties to moisture, solvents, chemical vapors, gases etc. Montmorillonite is a nanoparticle with anisotropic, plate–like, high aspect–ratio morphology. It is this morphology that leads to the improved permeation barrier through a tortuous path mechanism.

- The plastic matrix will have a higher heat distortion temperature. Only a few percent loading of montmorillonite will increase the temperature at which the plastic will begin to soften (glass transition temperature). This property is critical, for example, in under–the–hood automotive applications.
- This thermoplastic polymer is easily recyclable. Montmorillonite performance actually improves upon recycling. Fiberglass products typically cannot be recycled for the same application since; the fibers are damaged during the recycling process.
- This plastic can be dyed easily. Due to the colloidal nature, high surface area, and surface treatability of montmorillonite, it can serve as an active site to fix dyes into plastic.

1.5 Origin of the Proposed Study

Most of the reported literature shows that commercially used FRPs most generally use reinforcements like glass fibers, aramid fibers (e.g. Kevlar), carbon fibers, polymer foam and aluminium honeycomb; with epoxy, vinyl ester or polyester as the matrix. Poly(ethylene terephthalate) (PET) is a low–cost, and high performance thermoplastic that find applications in variety of areas such as in fabrics; soft drink bottles; reinforcement of tires and rubbery goods; food and beverage packaging etc. PET has excellent surface characteristics and high heat deflection temperature. PET which is reground from post consumed soft drink bottles have slightly reduced molecular weight and structure related properties as compared to pure polymer (Karabulut, 2003). Despite the various advantages and characteristic features offered by PET fibers, very limited work has been reported in open literature regarding use of PET fibers as reinforcement in FRP nanocomposites. This explains the origin of the proposed research work. Thus the proposed research problem is to fabricate and characterize a polymer based nano–composite with constituents as epoxy (matrix), organo–clay (nano-filler), and PET (fiber reinforcement).

1.6 Applications

Polymer based nanocomposites are of growing interest in the aerospace sector because of their high toughness, low–weight designs and low thermal degradability. Every pound saved in aircraft weight makes a massive contribution to payload, range and performance. The Boeing Dreamliner is the world's most efficient airliner and uses 32 tons of composites in its construction. This composite can be used for seat, interior, and also can replace outer body parts.

In automobile industry thermoset composites like BMC (Bulk Molding Compound) and SMC (Sheet Molding Compound) are widely used to replace under–hood components and enclosures such as valve covers, fuel hose, timing chain covers, oil drain pans, and intake manifolds.

In marine industry non–magnetic ship hulls, body of yachts, leisure boats and commercial fishing boats are preferred to be made up of fiber reinforced composite (Web reference: tifac.org, 2013). Also, improvements in thermal, barrier and mechanical properties have led to application of epoxy–clay nanocomposites in aerospace, defense and automobile industries. Similarily, adhesive, sealants, molding, casting, electronics and construction also finds the application of epoxy–clay nanocomposites (Azeez *et al.*, 2013).

Table 1.1 Applications of Polymer–Clay Nanocomposites (Camargo *et al.*, 2009)

NANOCOMPOSITE	APPLICATIONS
Polyimide/SiO2	Microelectronics.
PMMA/SiO2	Dental application, optical devices.
Polycarbonate/SiO2	Abrasion resistant coating.
PET/clay	Food packaging applications.
Thermoplastic olefin/clay	Beverage container applications.
Epoxy/MMT	Materials for electronics.
Polyimide/Clay	Automotive step assists - GM Safari and Astra Vans.

1.7 Summary of the Chapter

This chapter discusses the basic definition and necessity of the nanocomposite materials. The chapter throws light over the constitutional elements of these nanocomposite materials, their functions to be performed and answers the tedious question regarding the advantage of nanocomposites over conventional micro-composites. The chapter also comments on the property and benefits of constituents due to which they are preferred over other entities of their category. Finally the origin of the problem and the potential applications are discussed.

The next chapter presents literature review on polymer matrix based nanocomposites. The review has been restricted to epoxy resin based matrix systems with PET/ layered silicates as reinforcements. The literature review shall be used to discuss the effect of different constituents, methods of preparation, use of additives etc. on the mechanical and physical properties of polymer matrix nanocomposites.

Chapter 2

Literature Review

2.1 Literature review

This section presents the summary of work carried out by different researchers for improving the mechanical properties and other characteristics of PMNCs with epoxy as the matrix, PET as reinforcement and organically modified montmorillonite clay as the nano filler material.

Cioffi *et al.* (2003) fabricated PET/polymethylmetha acrylate (PMMA) composite using filament winding equipment with PET fibers treated with oxygen-plasma. Contact angle measurements were done to assess the PET surface modification tendency (indicating the adequate conditions for plasma treatment). Further tensile testing and SEM analysis were carried out to investigate the mechanical behavior and morphological changes with different treatment times.

PET fibers (13 μm diameter and 14 GPa elastic modulus) were treated in a cold plasma reactor for different time periods (0 s, 5 s, 20 s, 30 s, 100 s). Oxygen gas was used to produce the etching mechanism. Contact angle of fibers was measured using Rame-Hart goniometer. The composite PET/PMMA was fabricated using filament winding process and tensile testing of different samples was done using universal testing machine (UTM).

Non treated fibers exhibited 90º contact angle, which got reduced with increase in the treatment time, for 5 s and 20 s, respective values of contact angle were 31º and 7º (beyond 20 s time, no significant change in contact angle was observed).

The SEM micrographs indicated that an increase in treatment time upto 20 s resulted in higher adhesion between the fibers and matrix (5 s treated fiber showed no traces of matrix after failure whereas 20 s treated fibers had resin adhered to them after failure). However for greater exposure times (greater than 20 s), intense degradation of fiber surfaces was observed. Further, the average ultimate tensile strength values of the PET fiber/ PMMA matrix composite also improved for treatment time upto 20 s. However, maximum value was obtained for treatment time of 5s.

The authors concluded that the plasma treatment provided a reduction in the contact angle of fiber surfaces compared to the untreated fibers; consequently, this increased the superficial energy and the work adhesion of the PET fibers. The plasma treatment was responsible for stronger fiber/matrix adhesion, mainly after oxygen plasma treatment for 20 s. The average ultimate tensile strength of treated fiber composites exhibited higher values in comparison to the untreated fibers.

Isik *et al.* (2003) synthesized a nanocomposite comprising of epoxy resin, polyether polyol and montmorillonite (MMT) clay to evaluate the effect of impact modifier (polyol) on the morphological, thermal, and mechanical properties of the ternary system obtained, using XRD, SEM, DSC, and impact/ tensile tests.

The epoxy resin (DGEBA) was first cured with an aliphatic amine (hardener). The epoxy resin and MMT clay (varied as 0%, 1%, 3%, 5%) were mechanically stirred for 2 h at 35℃, followed by ultrasonic mixing for 30 min. Predetermined amount of polyether polyol (varied as 0%, 1%, 3%, 5%, 7%) was added to the mixture and mechanically stirred for an additional hour. The ternary system was cooled to room temperature and a curing agent, triethylenetetramine was added in the ratio of 100:20 (DGEBA/hardener) by weight. The slurry mixtures were poured into aluminium moulds and cured at 75 ℃ for 16 h followed by post curing at 130 ℃ for three hours more.

XRD analysis revealed that the impact modified epoxy resin (with polyether polyol, 7% wt. and MMT, 3% wt.) showed no significant change in interlayer spacing (basal spacing) as compared to nanocomposite without polyol (having only MMT, 3% wt.). It was concluded that polyol domains do not enter galleries between the clay layers. SEM micrographs of specimens having no clay and only polyol (1-7% wt.) showed that polyol forms an immiscible rubbery phase in the epoxy matrix. In polyol modified epoxy (with no MMT), impact strength was observed to be more with increasing amount of polyol, as the immiscible rubbery domains got populated. On the other hand, addition of polyol increased tensile strength but only upto some extent due to crosslinking of the system. However, as the polyol rich rubbery domains dominated there was a decrease in tensile strength due to stress concentration effect. Further, tensile strength, in general, was observed to decrease with increasing amount of MMT at constant polyol content. SEM analysis showed that presence of clay prevented uniform dispersion of polyol in resin, especially at high concentrations. DSC analysis showed that increased amount of clay and polyol increased the glass transition temperature, as clay and polyol interactions decreased the mobility of polymer chains.

Park and Jana (2003) investigated the mechanism of nanoclay exfoliation in epoxy-clay nanocomposite system and tested the hypothesis that the elastic forces (polymer recoiling) developed in clay galleries during epoxy curing is responsible for exfoliation of the clay structures. The epoxy-nanoclay system studied in this work included two types of epoxy molecules [an aliphatic (propylene glycol glycidyl ether) and an aromatic (DGEBA)], different curing agents, and different nanoclay treatments.

Organically modified clay particles: Clay1 (Cloisite® 30B, quaternary ammonium ion as the cation), Clay2 (Cloisite® Na^+) and Clay3 (Clay2 treated with n-hexadecylamine) were taken. Clay 1 and Clay 3 were separately intercalated by epoxy by stirring the ingredients at 80 ℃ for 6 h with a magnetic stirrer, and the resulting mixture was dried in a vacuum oven at 80 ℃ for 30 min. A stoichiometric amount of suitable curing agent was added to the epoxy-clay mixture and the ingredients were mixed further for approximately 5 min at 60 ℃. The resultant mixture was degassed in a vacuum oven for approximately 5 min at 60 ℃ and cured in an aluminum mold. The curable epoxy mixtures without the clay were prepared by mixing the ingredients for 5 min at 60 ℃. The curing temperature and time were varied as per curing agents.

WAXD (Wide Angle X-Ray Diffraction) results showed that quaternary ammonium ions increased the d-spacing in treated clay from 1.12 to 1.77 nm in Clay1 and to 1.92 nm in Clay3. It was observed that changing the sequence of curing agents and epoxy resins did not have much influence on the exfoliation behavior. The results presented elastic force as the primary force behind clay layer exfoliation in epoxy-nanoclay systems. The elastic force exerted by the cross-linking epoxy molecules inside the clay galleries pushed out the outermost clay layers from the tactoids against the opposing forces arising from electrostatic and Vander Waals attraction. Exfoliation continued until the extra-gallery epoxy turned into a gel (became highly viscous); on the other hand, the formation of gels was advanced by higher curing temperatures and presence of clay particles. It was found in this study that complete exfoliation of clay structures can be produced till elastic forces inside the galleries were prevailed by viscous forces offered by the extra-gallery epoxy.

Santos and Pezzin (2003) presented an experimental study on the composites with polypropylene (PP) as a matrix and recycled poly ethylene terephthalate fibers (rPETFs) as the reinforcement. Recycled PET was obtained from soft drink bottles and ropes. Composites of

PP/PET with 3, 5 and 7% of PET fibers (w/w) were prepared by extrusion followed by injection moulding and the mechanical behavior was estimated by the measurement of the tensile strength, the Izod impact strength and the surface hardness. The morphology was determined by scanning electron microscopy (SEM).

Recycled PET fibers (rPETFs) were incorporated in PP at 3, 5 and 7% (w/w) in the extruder. Temperature profile of the plastification cylinder was adjusted between 106 and 160 °C for the four heating zones, with an average rotation of 11.8 rpm, for all formulations. The extruded material was then cooled down to room temperature, was pelletized in a knife mill. The specimens for mechanical tests were obtained by injection moulding.

In the preparation of the composites, it was observed that the compositions with more than 10% (w/w) of rPETFs in PP presented degradation problems during extrusion, limiting to 7% the amount of rPETF to be incorporated in PP. The results of the tensile tests performed with the composites and the pure PP showed that the addition of rPETF in PP did not change significantly the tensile strength (increased by 3.7% with 5% of rPETF). Whereas, incorporation of the rPETF in PP dramatically decreased the elongation at break (around 82%) for all compositions.

For the Izod impact strength measurements, the results showed an increase in the impact strength for all compositions with rPETF (maximum change being 18.9% for 7% of rPETF). This could be due to the formation of agglomerates that acted as shock absorbing sites. The agglomerates with no ridges acted stress concentration points and facilitated propagation of cracks. This could have led to low elongation at break. There were no changes in the surface hardness of the composites, for all compositions, in relation to pure PP. This could be attributed to the low content of rPETF in relation to PP.

Chang *et al.* (2004) synthesized PET nanocomposites (using in-situ interlayer PET polymerization method) with different clay contents and draw ratios to evaluate the morphologies and resulting thermo-mechanical properties of the nanocomposite material.

To synthesize the C_{12}PPh-MMT/PET nanocomposite, the first step was to obtain organically modified MMT clay. For this, MMT clay ($MMT-Na^+$) and dodecyl triphenyl phosphonium chloride ($C_{12}PPh\text{-}Cl^-$, organic modifier) were mixed. Then 62 g of1, 2-ethylene glycol (EG) and 1.96 g of C_{12}PPh–MMT were placed in polymerization tube and the mixture was stirred for 30 min at room temperature. In a separate tube, 97 g of dimethyl terephthalate (DMT) and a few drops of isopropyl titanate (catalyst) were placed and this mixture was added to the organoclay–EG system, followed by vigorous stirring to obtain a homogeneously dispersed system. This mixture was heated first to 190 ℃ for 1 h. Then, the temperature was raised to 230 ℃ and the mixture was maintained there for 2 h. During this period, continuous generation of methanol was observed. Finally, the mixture was heated to 280 ℃ for 2 h and maintained at a pressure of 1 Torr. The product was cooled to room temperature, repeatedly washed with water, and dried under vacuum at 70 ℃ for 1 day.

The synthesized nanocomposites were hot extruded (at 270 ℃) to get fibers with different DRs and clay contents (clay content was increased from 0-3%). XRD results showed that addition of $C_{12}PPh\text{-}Cl^{-}$ (organic modifier) increased basal layer spacing significantly. Also, higher stretching of the fiber during extrusion led to better dispersion and exfoliation of clay. TGA results verified weight loss and increase in degradation temperature (maximum increase was 16 ℃ for 3 wt. %) with increasing the clay content. The observed increase in thermal stability was attributed to the fact that clay provided heat insulation effect. The tensile mechanical properties of fibers increased with increase in clay content. It was found that ultimate strength of fiber (3 wt % clay) increased to 1.5 times as compared to pure PET fiber. This improvement was due to the rigid nature of clay compared to PET molecules. Further, an increase in DRs resulted in decrease of ultimate strength unlike engineering plastics because high stretching's led to debonding and generation of voids.

Guan *et al.* (2005) synthesized a PET/MMT nanocomposite using in-situ polycondensation, converted the nanocomposite to fiber form using melt spinning and characterized the resulting fibers using XRD, DSC, TEM, TGA and tensile tests to evaluate their performance.

A suspension of sodium-MMT (1 part by wt.) in distilled water (40 parts by wt.), to which PVP (poly vinylpyr-rolidone 1 part by wt.) was dissolved, was stirred vigorously. The temperature was maintained at 90 ℃ for 4 h. Then the precipitate was filtered and washed with distilled water three times. The acquired MMT was dried in a vacuum to a constant weight at 80 ℃ and then grounded into powder. The obtained powder was uniformly dispersed in DMT (100 parts by wt.) and EG (72 parts by wt.). The catalyst (zinc acetate) was added to the mixture and was heated to 180 ℃. This resulted in generation of methanol and after its removal, the mixture was treated with antimony oxide (catalyst) and temperature was increased to 280 ℃. For acquiring the fibers, the nanocomposite was dried in a vacuum oven at 130 °C for at least 10 h. Now the melt spinning operation was performed and fibers were drawn.

TGA results showed that PVP treated MMT did not show any appreciable weight loss below 400 °C. XRD analysis showed that there was an increase in inter-layer spacing from 1.2 nm to 3.2 nm when untreated MMT was compared with PVP/MMT. Also, a strong shear stress during melt spinning caused MMT to exfoliate. However, it was observed that there were difficulties in processing of melt spinning with increasing amount of MMT. Further, for 5% elongation of PET/MMT nanocomposite drawn fiber, it was observed that MMT layers dispersed uniformly, restricting the movement of PET macromolecules and thus leading to increase in tensile strength. Also, the DSC results showed that heat shrinkage of the resulting nanocomposite got lowered, which was advantageous.

Teh *et al.* (2005) fabricated a composite of aromatic epoxy and PET (polyethylene terephthalate fiber) of diameter 20μm and length 2-3mm, 1 wt. % with the objective to investigate the fracture behavior and toughening mechanism of the composite for optimizing the treatment time required for surface modification of PET fibers with NaOH. The morphologies and chemical properties of the as-received composites and the ones with surface modified PET fibers were investigated by SEM and ToF-SIMS (time of flight secondary ion mass spectrometry) techniques.

For surface modification, PET fibers were subjected to alkaline hydrolysis with NaOH aqueous solution (50% w/v) at 80 °C for different time periods (0-30 min). Subsequently, the samples were washed with distilled water until all NaOH was washed away. ToF-SIMS technique was used to scan the surface topology and internal structure of the PET fibers during hydrolysis (surface modification) before adding them to the epoxy. All fibers were dried at 80 °C for 12 h in vacuum prior to mixing. The composites were prepared by mechanically mixing the short fibers with epoxy resin using a high speed homogenizer (at 700 rpm). Blends were degassed under vacuum and cured at 100 °C for 2 hrs. The mixture was then poured into a vertical glass mould and post-cured at 180 °C for 5 h. Samples of thickness 6.25 mm and width 12.5mm (ASTM E399) were taken for flexural testing (three point bending test) at room temperature.

SEM and ToF-SIMS investigations revealed that unmodified fibers showed smooth and featureless surface while the surface of modified fibers appeared with shallow pitting and some cracks for treatment time periods of 2.5 min. Fibers treated with NaOH for prolonged time, i.e. 20 min resulted in irregular surface and the fibers no longer remained straight.

The results also showed that fracture toughness of the neat epoxy increased by 33% upon addition of 1wt% untreated PET fibers and increased by 88% on addition of 1wt% treated (with NaOH for 2.5 min) fibers. On increasing the time of surface treatment, toughness decreased because prolonged alkaline hydrolysis led to large accumulation of pits resulting in crack initiation and internal hydrolysis.

Fractured surfaces of failed composites were also investigated with SEM. Observations revealed that non-treated fibers (Fig. 2.1) showed pullout, leaving clean holes in the epoxy, which represented poor adhesion between fibers and epoxy.

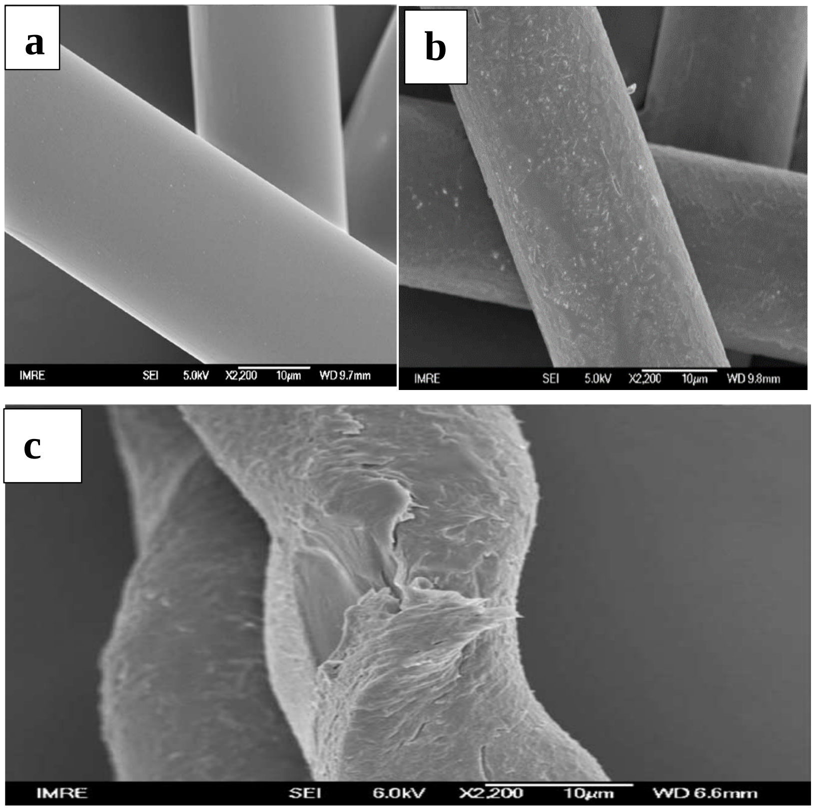


Fig. 2.1 SEM micrographs of (a) unmodified PET fibers (b) PET fibers with 2.5 min NaOH treatment (c) PET fibers with 20 min NaOH treatment (Source: Teh et al., 2005)

The fractured surface of the composite with treated fibers for 2.5 min (Fig. 2.2) showed typical breakage and river like structures on the surface, which indicated that a lot of energy was utilized during the fracture, while in the sample with treated fibers for a prolonged period (20 min treatment time), the river like structure was less apparent (Fig. 2.3), thus concluding that less energy would have been consumed.

Avila *et al.* (2006) synthesized fibre glass-epoxy-nanoclay laminate composites using vacuum assisted wet lay-up method and studied the impact strength and effect of nanoclay presence on damping behavior of the nanocomposites.

The nanocomposites containing (DGEBA and hardner triethylenetetramine in ratio 100:20), clay (OMMT) in different weight percent (1, 2, 5, and 10 wt. %) and S2-glass (laminates with 16 layers and 65% fibre volume fraction) were prepared by (vacuum assisted wet lay-up method). In this method, the nanoclay particles were mixed to acetone. These were blended into the hardener followed by degassing for an hour. The solution was then mixed to resin followed by stacking sequence and vacuum assisted wet lay-up lamination to form S2-glass/epoxy-nanoclay composites. It was then cured for twenty-four hours under vacuum at room temperature followed by low temperature co curing.

Impact test results indicated higher front face delaminated areas for the clamped condition as compared to the simply supported condition. Study of impact test as a function of energy levels showed that for energy levels of 15-22 J, the front face delaminated area was reduced (by 22%) with addition of 1 %wt. of nanoclay for both cases (clamped as well as simply supported) and the back face failure area and also the back face deflection were much smaller in nanocomposites as compared to neat epoxy; for impact energy levels of 25-36J, the back face delamination area got reduced by around 10% and the back face deflection got reduced by approximately 45%; for impact energy levels of 38-54 J, the back face failure area decreased by 21%, and its deflection was reduced by 20%. The back face failure area increased for clamped conditions which could be due to load concentration.

At energy level of 40 J for different nanoclay contents, specimens indicated that as the amount of exfoliated nanoclay increased, the damping also improved. Furthermore, analysis of rate of rebound force reduction showed that it was directly proportional to the amount of exfoliated nanoclay. However, it was observed that the optimum amount of exfoliated nanoclay was 5%. Higher nanoclay concentrations led to excessive stiffness which led to more rebounds.

The exfoliation of nano-sized clay increased the composite impact strength, as the damaged area decreased by approximately 20% for small amounts of nanoclay contents.

Choi *et al.* (2006) synthesized a PET/clay nanocomposite by directly intercalating a catalyst into the clay interlayers by metathesis reaction of sodium cations with chlorotitanium catalyst. Morphology and wide-angle X-ray diffraction of composites as well as gas and moisture transmission rate through the composite films were measured.

To prepare the clay-supported catalyst, MMT-Na clay was dried in a vacuum oven at 150 ℃ for 24 h before use. 10 g of MMT and 100 mL of anhydrous THF (tetrahydrofuran) were mixed for 2 h at room temperature. The catalyst, chlorotitanium triisopropoxide (2 g) was added to this suspension. The mixture was stirred for 24 h. The clay supported catalyst was isolated by filtration and was washed several times with anhydrous THF to remove unreacted catalyst. The weight of clay-supported catalyst obtained was 10.8 g. PET/clay nanocomposite was prepared by melt poly condensation in a small-scale batch reactor. 100 g of DMT (Di-methyl terephthalate), 64 g of EG (ethylene glycol), and 1 g of clay-supported catalyst were mixed. This mixture was first heated to 190 ℃ in a silicone oil bath and the temperature was maintained for 2 h. The temperature was then increased to 210 ℃, where it was maintained for 2 h. The reaction temperature was progressively increased to 280 ℃. Then the pressure was reduced to a specified level and maintained for 0.5–1 h. The thermal stability of clay-supported catalyst nanocomposite was more than simply catalyst added clay nanocomposite, as observed by TGA. WAXD results showed that peak of clay-supported catalyst nanocomposite got shifted to lower angle, as compared to MMT nanocomposite. Thus, it was concluded that catalyst increases the spacing between clay layers, and thus clay-supported catalyst (unlike organoclay) gives exfoliated nanocomposite, which results in good barrier properties (less permeable) in PET nanocomposites.

Khanchaitit and Aht-Ong (2006) fabricated a PET reinforced epoxy composite, using UV/ozone surface modification on PET fibers. The synergistic effects of UV and various gas species (nitrogen, air, oxygen, air/ozone, and oxygen/ozone) exposure as well as the effects of exposure time, i.e., 2, 5, and 10 min, on the morphology and chemistry of PET-fiber surfaces were investigated by using a scanning electron microscope coupled with energy dispersive x-ray analysis (SEM/EDX). The tensile testing and analysis of fractography of the resulted composites were performed to evaluate the effectiveness of the process.

The fiber samples used in this study were multifilament PET fibers. Each filament had an average diameter of 10 µm and surface modification was done in a 1 m long tubular stainless steel reaction chamber. The gas species were forced to pass through the center of the reactor chamber to give an increasing number of collisions of gas molecules on fiber surface. The epoxy resin and hardener selected were EPOTEC YD 582 and XDH 125 respectively. The two components were mixed as 3 parts of resin and 1 part of hardener by weight. The unidirectional specimens for tensile testing were fabricated by a casting mold in which PET fibers were 10% volume of the composite. The specimens obtained were based on the ASTM D 638 M standard. Vacuum environment was used to remove small bubbles which might be contained during mixing process. Tensile properties and morphology of PET fibers were investigated. The results indicated that both the gas species and the exposure time had no effect on the tensile properties of the samples. SEM micrographs revealed no significant changes in surface roughness upto micro level, however surface modification at nano level was observed. Hence, results suggested that any change in the tensile properties of the resulted composite should be affected by altering interface/interphase properties between the fiber and matrix, not by manipulating the fiber properties themselves.

Tensile test of PET/epoxy composite were carried out using universal testing machine equipped with 10 kN load cell. Tensile strength of composites carrying untreated fibers and treated fibers were compared. It was observed that untreated PET composite showed low mechanical properties. Composite carrying treated fibers for 5 min treatment time and UV/O_2 + O_3 gas specie showed most effective tensile properties with an increase of at least 25 MPa in tensile strength. When treatment time was increased upto 10 min, reduction in tensile properties was observed, and the possible reason that can be inferred was the formation of low molecular weight oxidized materials. SEM micrographs helped in drawing conclusions from the various failure mechanisms (like improvement in adhesion of the interface was observed, evidenced by the rough surfaces of the pulled-out fibers). Cracks were developed in epoxy matrix instead of the interface because of stronger interaction between the fiber and matrix.

Schmidt et al. (2006) evaluated technical sustainability of resin socket (termination) for deep-water mooring applications substituting some long-standing terminations. These consist of introducing a simple-ended rope (PET ropes 10 or 48 mm diameter) in a hollow metallic device having a conical shape and pouring into it a thermoset resin that once cured, fastens the rope extremity. Performance of socketed PET ropes was evaluated under tensile testing. The curing and visco-elastic behavior of various epoxy resin system was monitored with DSC and DMA.

Two kinds of PET ropes were used, 10 mm diameter for lab testing and 40 mm for pilot tests. The extremities of the PET ropes were inserted in the socket after dismantling yarn into a broom shape. The socket was secured in a vertical position with rope extremity inside it and pouring thoroughly mixed resin and hardener into the socket, starting from the base to the top avoiding any air bubble entrapment, and developing a continuous resin phase and the resin was allowed to cure for at least 7 days at room temperature. Also different epoxy/hardener systems were used.

The efficiency of the resins was evaluated by comparing average failure load of socketed and un-socketed rope on lab scale as well as pilot testing. Average failure load of 10 mm and 48 mm parent rope was recorded as 2348 kgf and 43,948 kgf respectively. The highest value of average failure load recorded for 10 mm socketed rope was 2714 kgf and for 48 mm socketed rope was 41,280 kgf. Though the results of failure were also the functions of resin type and socket dimensions where a perfect resin cone has not been produced in the inner socket surface.

The homogeneous distribution of resin infiltrating the rope extremity and volumetric ratio of resin to fiber (ratio greater than 5 gave adequate strength) were found crucial for optimized performance of the sockets. The glass transition of the fully cured resin (T_{g2}) was more dependent on hardener type than on resin type.

Gupta *et al.* (2007) synthesized bulk quantity of clay-epoxy nanocomposites using two different methods of preparation (mechanical mixing and shear mixing) to evaluate if the two processing methods resulted in different structure and mechanical properties (tensile, compressive, and impact properties) of the resulting nanocomposite. These properties were compared with those of the neat epoxy resin to observe the difference caused by addition of nanoparticles.

Five compositions of nanocomposites were synthesized containing nanoclay (Closite® 30B, MMT modified with a quaternary ammonium salt) in 0.125, 0.25, 0.50, 1 and 2 vol. %. These composites were synthesized both by mechanical as well as shear mixing methods. The ratio of epoxy resin (D.E.R. 332), amine based hardener (D.E.H. 24) and diluent (C_{12}–C_{14} aliphatic glycidyl ether) was taken as 83.5:4.4:12.1 (% vol.) in all specimens. The first mixture was prepared by mechanical mixing in which the mixture was stirred at 650 rpm for 2 h at 50 ℃. The composite slabs were cast in aluminum molds, cured for 24 h at room temperature and then post cured at 100 ℃ for 3 h. The processing was carried out with 4 lt. of resin in each batch. Similar mixture was prepared by shear mixing method using a three step process. First, the desired volume fraction of nanoclay was added to the epoxy-diluent mixture and hand stirred. Then, the mixture was placed under the drill machine and mixed at 650 rpm for 30 min to obtain homogeneous distribution of nanoclay within the resin. The mixture was then shear mixed using a three roll mill at 180 rpm.

XRD results showed that nanocomposites synthesized using mechanical mixing had exfoliated nanoclay, whereas in shear mixing, only intercalation of the clay was observed. The mechanically mixed specimens with exfoliated nanoclay exhibited a higher modulus than the shear mixed specimens. The impact strength for nanocomposites was higher for mechanically mixed specimens, but lower than the neat epoxy resin.

Further, mechanical testing (tensile, compression and impact) results showed that the tensile and compressive modulus increased with increase in clay content. The tensile modulus showed maximum improvement i.e. increase of about 50% with addition of 2 vol. % nanoclay. The possible reason was that clay hinders the movement of epoxy in its vicinity. The maximum strength was exhibited by 0.25 vol. % nanoclay specimens and thereafter the strength decreased.

Hwang *et al.* (2008) synthesized nanocomposites prepared by in-situ polymerization process to observe the dispersion of MMT clay (both, unmodified and alkyl modified A10-MMT clay) within the PET matrix to compare performance in terms of mechanical and morphological properties of the two types of nanocomposites.

PET nanocomposites containing pristine and organically modified MMT (0.5–2.0 wt. %) were prepared by in-situ polymerization. In an esterification tube, 62 g of EG (Ethylene glycol), 0.97 g of organically modified MMT (1 wt. %), and Zinc acetate (0.0172 g) were subjected to ultra-sonication for 30 min. During vigorous stirring, 97 g of DMT was added to the EG slurry to obtain a homogeneously dispersed system. The mixture was then heated for 30 min at 100 ℃ and was raised to 150 ℃. The temperature was raised further to 210 ℃ to initiate esterification between silicate layers in the clay. The ester exchange reaction was carried out for 3 h while continuously removing methanol. Finally, polycondensation was performed below 0.1 Torr at temperatures between 180 and 285 ℃ with 0.0084 g of antimony (III) oxide catalyst. The resulting nanocomposites were repeatedly washed with water and dried under vacuum for 24 h at 80 ℃. The sample films (20 cm×20 cm×0.3 mm) were prepared by a heating press.

X-ray diffraction (WAXD) indicated that A10-MMT facilitated higher level of intercalated PET than Na^+-MMT. At the same level of clay content, clay particles in PET/ A10-MMT exhibited a higher degree of exfoliation and were more uniformly dispersed throughout the PET matrix, compared with clay particles in PET/ Na^+-MMT. The degree of exfoliation was determined by TEM measurements, which showed clear separation between the silicate layers of the clay. SEM images of the nanocomposites confirmed that the alkyl modifier of A10-MMT significantly improved the compatibility between PET and MMT. The mechanical properties of PET/A10-MMT were superior to those of PET/ Na^+-MMT. The degree of dispersion of clay into the PET matrix was the main factor responsible for the enhancement of mechanical properties regardless of the clay content. The alkyl modifier in A10-MMT therefore provided not only enhanced exfoliation and PET compatibility, but also improved mechanical properties.

Hadjizadeh *et al.* (2010) analyzed the effect of NaOH treatment provided to melt blown non-woven PET structures (PET mats with small diameter fibers, <10 μm) for evaluating the morphological, physical and mechanical properties as a function of treatment duration and fiber diameter. The main techniques used were DSC, SEM and tensile testing.

PET fibers were synthesized using melt blowing process (6 μ and 10 μ). PET mats were fabricated on homemade pilot plan setup. PET extrusion was performed through a die and exposed to high speed hot air streams through a narrow gap sidewise of the die which resulted in stretching of the fibers and then made fiber networks. The produced webs were collected on a rotating drum. Individual web layers were placed on a 4 mm thick aluminium plate and then the plate was wrapped into a high temperature vacuum bag using a standard bagging procedure. The consolidation process was performed in an oven under controlled temperature (90℃) and vacuum (-25 in Hg) for 30 min. The PET mats were cut into square pieces (3×3 cm / 5×5 cm) and soaked in NaOH solution (2 ml NaOH of 1normlity per 1 cm^2 of mat) in a glass container. The matrices were treated for different durations (20 min, 40 min, 60 min, 2 h, 4 h and 24 h) at temperature of 65℃. Then these were thoroughly rinsed with deionized water and allowed to dry in ambient condition for at least 24 h.

It was observed that with increase in treatment time, the hydrolysis rate of samples increased which led to weight loss (weight loss experienced by the smaller diameter fibers was higher). The surface density of the woven mats increased with treatment duration ranging from 20 min to 2 h, but started decreasing with further increase in treatment duration. The smaller diameter fiber mat (thickness 156 μm) resulted in more variation in the tensile properties than the larger diameter fiber mat (thickness 208 μm). For both the mats, by increased treatment duration, Young’s modulus and tensile stress decreased but tensile strain increased. This suggested that by an appropriate matrix design and treatment condition optimization, it is possible to alter and obtain better mechanical properties.

Nagalingam *et al.* (2010) developed FRP with eight different combinations of polyester resin (epoxy), emulsion fiber (thickness 300 micron) and nano-powder (colloidal silica) using layered manufacturing technique (LM) and measured the mechanical properties. The amount of nano-powder was varied from 2–10 % (i.e. 2%, 4%, 5%, 6%, 8% and 10%) and fiber from 20–30 % (i.e. 20%, 22%, 24%, 25%, 26%, 28% and 30%). The combinations were summarized in Table 2.1.

The tensile strength, impact strength and fatigue life of an experimentally produced nanocomposite FRP in various combinations of polyester resin, fiber and nanopowder was investigated at room temperature. Tensile tests were performed according to ASTM D 638 at a test speed of 50 mm/min.

The nanocomposite fiber reinforced plastic had shown significant changes in properties which are compared against the composite (70% resin and 30% fiber) containing 0% nanopowder. Results showed sufficiently high ultimate tensile strength and 23% improvement of ultimate tensile strength at 5 wt. % increment of nanopowder. Impact strength increases to 10 J/mm^2, on an addition of 10 wt. % of nanopowder. Fatigue life increases to 14×10^5 cycles for the increment of 6 wt. % of nanopowder and 24 wt. % of fiber. The above three parameters of this study which can predict the influence of nanoparticle in FRP greatly increase tensile strength, impact strength and fatigue life.

Table 2.1 Combination of polyester resin, fiber and nano-powder (Nagalingam *et al.* 2010)

Combinations	Weight Percentage (%)	Weight (g)
Polyester resin Fiber	70 30	1050 450
Polyester resin Fiber	75 25	1125 375
Polyester resin Fiber Nanopowder	70 28 2	1050 420 30
Polyester resin Fiber Nanopowder	70 26 4	1050 390 60
Polyester resin Fiber Nanopowder	70 25 5	1050 375 75
Polyester resin Fiber Nanopowder	70 24 6	1050 360 90
Polyester resin Fiber Nanopowder	70 22 8	1050 330 120
Polyester resin Fiber Nanopowder	70 20 10	1050 300 150

Chakradhar *et al.* (2011) synthesized a high strength and low cost nanocomposite for making light weight components for automobile parts etc. by blending epoxy (Ardalite-LY 556) with unsaturated polyester (Ecmalon 9911) (i.e. 85/15 % w/w ratio) and adding montmorrilonite (MMT) clay ($H_2Al_2O_6Si$) whose quantity was varied between 0% to 5% by weight (0%, 1%, 2%, 3%, 5%). Addition of unsaturated polyester was done to reduce overall cost. Mechanical properties like tensile strength (TS), impact strength (IS), and inter-laminar shear strength (ILSS) were investigated as a function of clay content in the nanocomposites. Thermal characteristics like thermal decomposition behavior and glass transition temperature were also evaluated using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). SEM and TEM analysis were also performed to observe the distribution of secondary phases and the fracture type in the nanocomposite.

Epoxy/polyester and clay (dried in oven at 80°C for 24 hours) were mixed in pre-calculated amount using mechanical stirrer. Stirring was done thoroughly for about one hour at ambient conditions. The mixture was placed in a high intensity ultra-sonicator for about one and a half hour in an ice bath in order to avoid temperature rise. Sonication was done to achieve uniform distribution and exfoliation of clay layers. After completion of sonication, other constituents viz. hardener/accelerator/catalyst/promoter were added (in weight proportion 100:10/2/2/2 respectively) to the epoxy/polyester mixture. The mixture was then poured in a glass mould in order to get samples according to ASTM standards.

The results revealed that by increasing the clay amount to an optimum level (3 % by weight), the TS, IS, ILSS increased by 30%, 16%, and 52% respectively with respect to the neat blend without any clay content. This was due to the excellent adhesion and interfacing between the clay layers and the epoxy/polyester. However, when the clay content was increased beyond 3%, a fall in mechanical properties was observed. It was concluded from the morphology of fractures, analyzed by SEM and TEM (Transmission electron microscope) that further increase in clay content caused agglomeration, which results in a lower aspect ratio with a consequent decrease in stress sharing by clay agglomeration.

Thermogravimetric analysis revealed that thermal stability of the composite improved with increased clay content with 15% weight loss observed for 5 wt. % clay sample. Also a 10 ℃ rise in decomposition temperature was obtained compared to a neat blend. Differential scanning calorimetry showed that clay particles increased the glass transition temperature by 3 ℃ for 3% clay content. The clay particles opposed the movement of matrix in its vicinity when the nanocomposite is subjected to shearing.

Jindal (2013) synthesized a nanocomposite with epoxy resin as base and MMT clay (nanoclay Closite® 30B), and Recron® fiber PET (Polyethylene terephthalate) as the reinforcement and investigated the change in mechanical properties by varying only the amount of PET fiber. The PET fibers used were of 15μm diameter and 3mm length. Laboratory synthesis of nanocomposite was done by simple hand lay-up process. The nanocomposites consisted of MMT clay (3% by weight), PET fiber in different weight ratios (0%, 0.25%, 0.5%, 0.75% and 1%) and the epoxy resin. Also, while preparing the composites, the PET fibers were dipped in NaOH solution (for

2.5 min and rinsed thoroughly by distilled water) to roughen the fiber surface and facilitate the interfacial bond of fibers with the matrix.

The mechanical properties investigated include tensile properties (ultimate tensile strength, modulus of elasticity), bending strength, impact strength and microhardness. These properties showed an appreciable change with change in PET fiber content. Structural analysis was also conducted using XRD and SEM to observe the distribution of clay.

The results showed that ultimate tensile strength of the nano-composite increased by increasing percent weight of PET fibers upto an optimum level (0.5% PET) and thereafter decreased gradually. Modulus of elasticity decreased continuously with an increase in PET fiber. Bending strength and impact strength showed a continuous increase with increase in PET fiber content. Toughness of composite further increased in the NaOH solution treatment. Microhardness decreased with an increase in PET content. All the results showed that PET imparts ductility to the composite. XRD results showed that epoxy chains were intercalated into the nano-clay layers. There were a few limitations in this work. Only one parameter i.e. PET content was changed and that too upto 1% only. Though X-Ray diffraction and SEM analysis were conducted, the structural-mechanical property relationship for nanoclay and PET fiber was not discussed.

Liu *et al.* (2013) adapted the technique of surface modification using ultraviolet radiations and compared it with other techniques like corona discharge (CDT) and alkaline treatment. The fabrication of composite is done using the laminates of PET fabric and TPU (polyurethanes).

PET fabrics were dipped in acetone/H_2O solution of various concentration and irradiated under UV (1 kW light generated from CVT-0055) for 15 min and then washed with deionized water. After vacuum drying, the treated fabric was dipped in a toluene solution and sealed for moisture-proof at room temperature. After 12 h the fabric was taken out and baked at 120 ℃ for 1 h, rinsed with acetone and vacuum dried.

The adhesion between TPU and PET fabric was measured using T-peel test of the laminates. The mechanical properties are evidently dependent on the kind of treatment. The fibers modified with sodium hydroxide solutions show a clear decrease in tensile strength and elongation, especially high in the case of fibers treated with NaOH (16 wt. %, 80 ℃, 120 min). CDT shows an advantage in the retention of the mechanical properties, without any distinct loss of fiber tensile strength and elongation at break.

Adhesion between PET and TPU was improved by grafted PET fabrics obtained using UV treatment. This treatment provides matrix friendly surface to the fibers. The good adhesion is achieved through covalent chemical bonding, acid–base interactions or hydrogen bonding, fiber and resin surface energies that favor complete wetting of the fibers by resin, large specific surface area of fibers, and surface roughness that allows key and locks type mechanical bonding were the advantages provided by this treatment.

2.2 Summary

From the literature review, it has been found that addition of nano–size filler and micro–size fiber to epoxy based polymer matrix results into improved properties as compared to those achieved in the conventional composite systems. Further, surface treatments provided to the fillers/ fibers have been reported to show impact on the morphology and properties of nano–composites. Some salient observations from the literature review are presented below:

A. Several authors have investigated the improvement in mechanical properties resulting from changes in nano–filler content in the epoxy/ polyester matrix based nanocomposites. The tensile modulus, compressive modulus, tensile/ compressive strengths have been reported to show significant changes with different clay loadings. Authors have conducted experiments to find the specific levels of clay loadings which could provide an optimum combination of the properties (Isik *et al.*, 2003; Gupta *et al.*, 2007; Chakradhar *et al.,* 2011).

B. Chemically modified PET fibers treated with NaOH solution improved the interfacial interactions between the matrix and fibers. The surface modification conditions were optimized by changing the treatment time. Treatments resulted in chemically reactive fiber surface which improved fiber-matrix adhesion and significantly improved mechanical properties (Teh *et al.*, 2005; Hadhjizadeh *et al.,* 2010).

2.3 Limitations in the Existing Literature

The study of nanocomposites is one of the distinguished fields of research where mechanical and chemical engineering work together on various methods of fabrication using different constituents; surface treatments methods; curing times and temperatures etc. so as to achieve objectives like enhanced physical, chemical, and mechanical properties along with light weight.

The proposed study has specifically reviewed literature on PMNCs using PET/ clay in an epoxy matrix system. The study describes the work carried out by different researchers in the area of enhancing the composite's characteristics. Despite the extent of work reported in the field, some gaps and limitations have been found, leading to the development of scope of work in this area. The major limitations in the existing literature are reported below:

- Very limited work has been reported on PMNCs composed of epoxy (as matrix), PET fibers (as reinforcement) and Clay (as nano-filler). There is still a scope of work required to be done for obtaining a judicial combination of these constituents, leading to improved mechanical properties.
- A few authors have reported about surface modification techniques, used for PET fibers, for improving interfacial interactions between the matrix and fibers, leading to enhanced interfacial adhesion. Literature lacks in comparative analysis of various surface modification techniques with regard to improvements in mechanical properties of resulting composites.
- The alkaline treatment (using NaOH) of fibers is one of the surface modification techniques. However, literature lacks any information regarding the concentrations of alkaline solution to be selected for treatment along with treatment temperatures and time periods. More detailed work needs to be done with regards to the optimal surface modification conditions resulting in improved mechanical properties.
- Exfoliation of the filler material (MMT Clay) in the epoxy matrix is one of the important phenomena whose occurrence leads to improved mechanical properties. Literature reports various parameters, used by different researchers, for increasing the extent of exfoliation. These include using different curing agents, curing temperature etc. There is still a lack of study attempting to systematically combine these parameters to obtain optimum values for each parameter, which could result in the best exfoliation.

Chapter 3

Design of the Study

3.1 Introduction

This chapter brings forth the details of design of the proposed study. The chapter describes the properties of constituent materials used to fabricate the composite, the method of fabrication, compositional details, and the process parameters which helped to achieve the objective.

3.2 Establishment of Objective Function

The review of literature for the present study showed that several studies have been done on polymer based nanocomposites having reinforcements like carbon nanotubes, glass, kevlar, elastomers, etc. However, limited literature was available on enhancement of mechanical properties of nanocomposites mainly comprising of epoxy (thermosetting) as the base, PET (thermoplastic) as the fiber reinforcement and organic clay (OMMT-clay) as the nano-filler.

The main objective of the present study is to evaluate the mechanical properties (especially tensile and flexural properties) of an epoxy-hardener system by addition of both a micro and a nano-filler. In the present work, PET has been used as the micro-filler and OMMT clay has been used as the nano-filler. Also, in the present work, the PET fibers have been subjected to surface modification in order to change their surface morphology for enhancing interfacial adhesion between fibers and matrix. So, the present work also investigates the effect of surface modification of reinforced fibers on the performance of nanocomposites system. The overall objective of the present work is to evaluate *the mechanical properties of nanocomposites at different concentration levels of micro and nano fillers and to obtain the surface modification procedure for improved properties.*

The key issues taken up during the proposed work are as follows:

- Fabrication of nanocomposites with different compositions to evaluate changes in properties with change in concentration of constituents. Thus, to evaluate the effect of each constituent on specific properties.

- Surface modification of PET fibers with alkaline solution (under varying conditions of temperature, and time for a given concentration of solution) to determine the surface modification conditions resulting in improved properties.

The present work involves characterization for the following:

- ➢ XRD analysis to determine the extent of dispersion of nano-filler in the matrix (distribution of secondary phase).
- ➢ SEM analysis to evaluate the surface topology of treated/ modified fibers.

3.3 Methodology

The methodology of the present study comprised of two main phases:

3.3.1 Methodology for Phase I

This phase was aimed to determine the effect of amount of PET, clay and epoxy needed to fabricate a nanocomposite on the resulting mechanical properties. In this phase, PET fibers were used in the as-received state (i.e. without any surface modification). The literature available on this specific combination of constituents is extremely limited due to which the optimum composition is still a matter of deliberation. The range of the amount of nano-filler and fibers to be used in fabrication of nanocomposites was obtained from the existing literature.

Phase 1 involved the following:

- Fabrication of nanocomposites with different weight concentration of constituents (epoxy, nanoclay and PET) using the hand lay-up technique. The different compositions for the PMNC system were determined through the ‘Mixtures Design’ module of ‘*Design of Experiments*’ approach. The details have been shown in Table 3.1. Here, in this phase, the PET fibers were not surface treated and were used only in the as-received form.
- Determination of mechanical properties (tensile and flexural strength, flexural modulus) of the resulting nanocomposites.

3.3.2 Methodology for Phase II

In Phase II of work, the effect of surface modification of PET fibers on resultant properties of nanocomposites was investigated. In this important phase, surface modification of PET fibers using an alkaline treatment was done with the aim to increase the interfacial adhesion between PET fibers and epoxy matrix. Phase II involved the following:

- Surface treatment of PET fibers under different conditions was done. PET fibers were treated with an alkaline solution of a fixed concentration. Different conditions comprised of subjecting the fibers to surface treatment at different temperatures and with different holding times at a given temperature. The treatment conditions for the present study (conditioning time and treatment temperature combinations) were formulated based on the existing literature.
- Characterization of the treated fibers was done to select the ones (treatment conditions) which responded favorably to the surface treatment. SEM images were obtained to observe changes in the surface topology of fibers. These SEM images were compared with the SEM images from available literature on similar work to select the treatment conditions showing potential to improve adhesion between fibers and matrix.
- Fibers treated under these selected conditions were used to again fabricate the nanocomposite system.
- Determination of mechanical properties of the resulting nanocomposites to determine the best treatment conditions for PET fibers in the present case. The optimum conditions were in terms of the optimal surface treatment time and temperature of the alkaline solution.

3.4 Material Selection

This section describes the constituents (of the nanocomposites to be fabricated) with regards to their characteristics, properties, concentration range etc. to be used in the proposed work.

3.4.1 PET (Poly ethylene terephthalate) Fibers

Thermoplastic polymer fibers, **Recron® 3s** (Supplier: *Reliance India Limited*, India) were used as the micro-filler fiber reinforcement in the present study. Recron® 3s is an engineered micro-fiber which is thermally stable and its properties do not deteriorate upon exposure to moisture. It has a unique triangular cross-section and is conventionally used as a secondary reinforcement in concrete. It complements structural steel in enhancing concrete's resistance to shrinkage cracking and improves mechanical properties such as flexural/split tensile and transverse strengths of concrete along with the desired improvement in abrasion and impact strengths (Web reference: http://www.ril.com)**.** Researchers have been experimenting with the addition of fibers in epoxy matrix to come up with a potential composite to replace other conventional composites in terms of mechanical properties and cost effectiveness. Some of the characteristics of PET fibers (especially Recron® 3s) are as follows (Parul, 2013; Web reference: http://www.ril.com).

- Recron® has excellent unmatched dispersion in water. This gives uniform three-dimensional dispersion throughout the matrix.
- Recron® 3s is proven for its performance in various wet-laying technologies.
- Recron® 3s gives a unique crimp for better locking inside the matrix.
- PET provides good temperature stability (melting point > 250 ℃), making the product dimensionally stable under curing conditions.

3.4.2 OMMT Clay

Among the different type of clay minerals, MMT is the most commonly used for preparation of PMNCs. MMT owes special attention among its group due its ability to show extensive inter layer expansion or swelling, because of its peculiar structure. The silicate layers of MMT are planar, stiff about 1 nm in thickness with high aspect ratio and large active surface area (Azeez *et al.*, 2013). The main reason for the remarkable improvements observed in polymer/layered silicate nanocomposites is the stronger interfacial interaction between the matrix and the silicate. The use of nanoclay improves surface area to volume ratio which allows more sites for bonding, catalysis or reaction with surrounding material (Alexandre and Dubois, 2000; Camagro *et al.*, 2009).

3.4.3 Epoxy Resin

Epoxy-hardener system used in the present work was of *Araldite family (epoxy: GY 257, hardener: HY 837;* Suppliers: *Huntsman Advanced Materials, India*) having a viscosity 5–6.5 poise at 25 ℃. Araldite has good mechanical properties and chemical resistance. It is strong and waterproof, making it an ideal bonding solution for load bearing or exterior use. The properties of araldite can be varied within wide limits by using different hardeners and fillers. Due to the low density, good adhesive and mechanical properties, epoxy resins have become a promising material for many high performance applications (Chow, 2007; Kotsilkova, 2007).

3.5 Input Parameters

The input parameters for the present work and their concentrations in the fabricated nanocomposites are discussed as follows:

3.5.1 Concentration of PET Fibers

PET fibers in the present study were varied in the range 0–1.5 wt. % of the nanocomposite system. This range was obtained from earlier studies of Teh *et al.* (2005), Jindal (2013), and Parul (2013). All reported studies on epoxy based nanocomposite systems contained a maximum of 1.0 wt. % of PET fibers in the fabricated nanocomposite systems. In the present work, the range has been slightly extended to upto 1.5 wt. %.

3.5.2 Concentration of Clay

Organic clay as a nano-filler plays a vital role in enhancing the mechanical properties. Though, it is one of the important constituents but its increased amount can also impair the mechanical properties due to agglomeration and/ or other problems. Thus, deciding the clay amount was one of the important considerations in the study. For the present research work, clay amount was varied in the range 0–2.25 wt. % of the nanocomposite system. This range was obtained from earlier studies of Park and Jana (2003), Gupta et al. (2007), Hwang et al. (2008); Nagalingam et al. (2010), Chakradhar et al. (2011), and Amendola et al. (2012). In most of these studies, it was reported that increasing the amount of clay beyond 3 wt.% caused agglomeration, which either caused crack initiation or propagation. Thus, the maximum clay content was restricted to 2.25 wt.% in the present work.

3.5.3 Concentration of Constituents in the Nanocomposite

Nanocomposites with different weight concentration of constituents (epoxy, nanoclay and PET) were fabricated in the present work. The different compositions for the PMNC system were determined through the 'Mixture Design' module of '*Design of Experiments'* approach. Minitab software (Minitab17; Minitab Inc., PA, US) was used for design of experiments. Mixture design is one of the main type of DOE applications concerning the preparation of mixtures. The mixture design supports experiments with factors that are ingredients in a mixture. The properties of a mixture are a function of the relative proportions of the ingredients rather than their absolute quantity. In experiments with mixtures, a factor's value is its proportion in the mixture, which falls between zero and one. The sum of the proportions of all constituents in a mixture design is one (100%). One has to choose a mixture design for the experimental work which is appropriate for the problem i.e. simplex centroid, simplex lattice, or extreme vertices mixture design. Extreme vertices design covers only a sub portion or smaller space within the simplex. The presence of both lower and upper bound constraints on the components create this condition to choose extreme vertices design and thus it was chosen for obtaining the experimental runs for the present study. The goal of an extreme vertices design is to choose design points that adequately cover the design space.

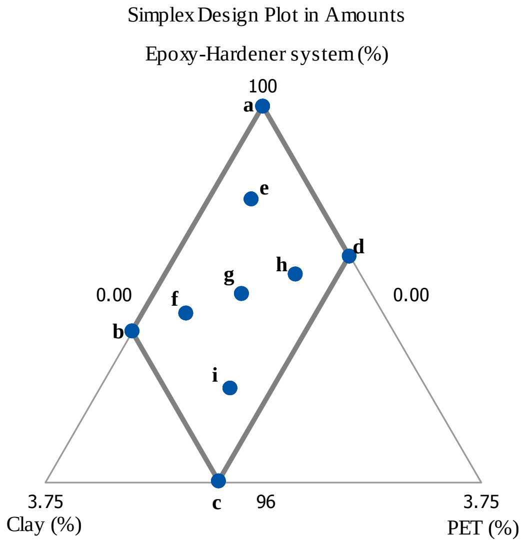


Fig. 3.1(a) Extreme vertices design

Figure 3.1(a) shows the extreme vertices for three component design with both upper and lower constraints (maximum clay and PET content in the present work is 2.25 and 1.50 wt. % respectively). The extreme vertices of the quadrilateral “abcd” represent the lower and upper bound constraints on the components and the area represents the design space. The points a, b, c and d are put at the extreme vertices of design space whereas f, g, h and i represent the average of extreme points. The proportionate values of the design points are described in Table 3.1.

Table 3.1 Mixture design for the experimental work

Run order → ↓ Constituents	1 (b)	2 (i)	3 (a)	4 (g)	5 (d)	6 (e)	7 (c)	8 (f)	9 (h)
Epoxy/Hardener (wt. %)	97.750	97.188	100	98.125	98.500	99.063	96.250	97.938	98.313
Clay (wt. %)	2.250	1.6875	0	1.125	0	0.5625	2.250	1.6875	0.5625
PET Fibers (wt. %)	0	1.125	0	0.750	1.500	0.375	1.500	0.375	1.125

3.5.4 Treatment Conditions for Surface Modification of PET fibers

A few authors have worked on the surface modification of PET fibers to enhance their performance in the nanocomposite systems. Available literature includes the work of Cioffi et al. (2003), Teh et al. (2005), Khanchaitit and Aht-Ong (2006), Hadjizadeh et al. (2010), Donelli *et al.* (2010), Blazquez et al. (2013), and Liu et al. (2013). In these reported studies on surface modification, Teh et al. (2005), Hadjizadeh et al. (2010) and Donelli et al. (2010) have used alkaline treatment. In the present work, surface modification of PET fibers through alkaline treatment has been done. The range of process parameters has been selected from the available literature. Alkaline treatment is done in order to modify the morphology of the surface of PET fibers and to reduce the chemical inertness leading to better adhesion, both mechanically and chemically. However, extensive exposure to alkaline solution can also deteriorate the fibers by driving cracks into the fibers. NaOH is the most commonly used alkali for treatment of polymer fibers. The treatment time is also a function of temperature and concentration of solution. Teh et al. (2005) fabricated epoxy based composites reinforced with PET fibers. The fibers were treated with NaOH (50 g of NaOH in 100 ml of water) at 80 ℃ for different treatment times of 2, 2.5, 5, 10, 15, 20 min respectively. The present work also uses the same concentration of alkaline solution (50 g of NaOH in 100 ml of water i.e. 50% w/v ratio) with almost same treatment time periods (2.5–15 min). The treatment conditions have however been extended by using different temperatures. Treatment has been conducted at ambient conditions (31 ℃) to check the possibility of surface modification at room temperature itself. Surface treatment was also carried out at 50 ℃ (temperature high enough but below the glass transition temperature). Finally, treatment was conducted at 80 ℃ (temperature above the glass transition temperature and also reported in literature).

The surface modification parameters (time and temperature) were varied as per data given in Table 3.2.

Table 3.2 Surface modification parameters for PET fibers

S. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature (℃)	31	31	31	31	50	50	50	50	80	80	80	80	80	80
Time (min)	2.5	5	10	15	2.5	5	10	15	2.5	5	10	15	30	45

3.6 Experimental Equipment and Facilities

This section provides an overview of the various machines and equipment used in the present study for fabrication, characterization and testing of the composites.

3.6.1Homogenizer

The equipment facilitates the homogeneous dispersion of nanoclay in the resin. Dispersing is the mixing of at least two substances that, hardly dissolve in each other, or don't chemically react with each other. During a dispersing process, one substance (dispersing phase) is distributed throughout another substance (continuous phase).

Homogenizer system (Make: IKA T26 ULTRA-TURRAX, Cole-Parmer, Chicago, US) shown in Fig: 3.1 was used during the fabrication of the composite. The set-up is available at Chemical Engineering Department, Thapar University, Patiala.

Dispersing using this equipment is based on the rotor-stator principle. Here, the rotor is moved with a high circumferential speed. The rotation produces suction, which pulls the medium into the rotor and then pushes it to the outside with help from the stator's teeth. This process results in the sample's dispersion**.**

Fig. 3.1 Homogenizer system dispersing clay in the resin

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.6.2 Probe Sonicator

The probe sonicators are the most effective units for nanoparticle applications. They are generally used to agitate the nano-filler dispersed in the resin, so that the former does not settle down before solidification of the nanocomposite system during fabrication. These can be used with a variety of powerful probe options which can process samples quickly and effectively. Probe sonicator (Make: Q Sonica Sonicators, Newtown, US) shown in Fig 3.2 was used during the fabrication of the composite. The set-up is available at Chemical Engineering Department, Thapar University, Patiala.

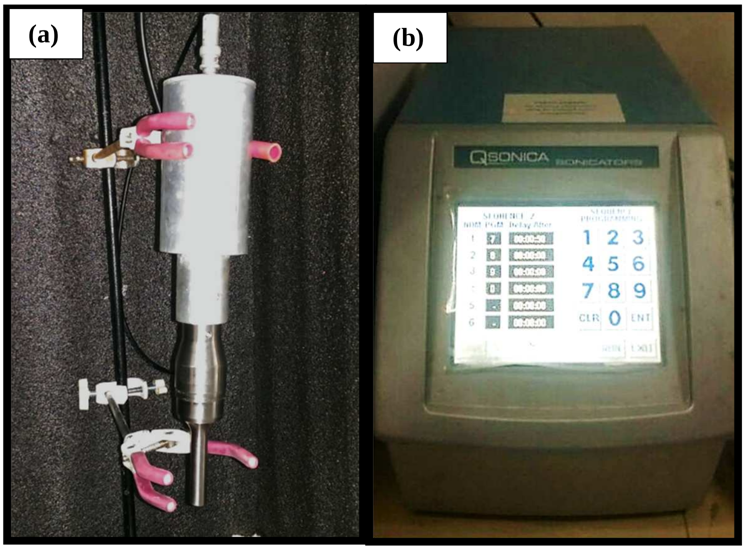


Fig. 3.2 (a) Probe sonicator (b) micro-tip controller

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.6.3 Mechanical Stirrer

After the nano-filler (clay, in the present work) has been dispersed in the resin, the mixing of fibers and finally of the hardener is done. Mechanical stirrer is required for the mixing of fibers, hardener etc. into the resin system. Mechanical stirrers are specially designed for a broad spectrum of applications requiring low speed and high torque for stirring of viscous fluids and materials. They are suitable for intensive mixing in laboratories and pilot plants. The stirrer comes equipped with a protection for overheating of the motor by means of self-locking temperature limiter. The user has a choice of different types of drives i.e. AC drive, AC/DC drive and PMDC with step-less speed regulations for continuous variation of speed as per the requirements. Mechanical Stirrer (Make: REMI Laboratory Instruments, Mumbai, India) shown in Fig: 3.3 was used during the fabrication of the composite. The set-up is available at Chemical Engineering Department, Thapar University, Patiala. The working speed of the equipment is adjustable upto 2400 rpm, with the shaft diameter (ϕ) of 8 mm and overall length of 400 mm. The mechanical stirrer is featured with digital speed display, adjustable speed agitator shaft, and a robust and ergonomic design with quiet operation.

Fig. 3.3 Mechanical stirrer

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.6.4 Oil Bath

An oil bath provides a uniform source of heat whose temperature can be closely controlled in comparison to other heating devices. A laboratory oil bath is made of an aluminum or stainless steel pan, a heavy porcelain dish or thick walled glass to withstand breakage and accidental spill. Mineral oil is typically used for oil baths in research labs for reactions that require heating temperatures upto 200℃ and above. The only disadvantage of an oil bath is the long time required to bring it to the desired temperature, splattering if it gets contaminated with water and the possibility of spilling of the hot oil. The electric heating coil is controlled using a variable voltage controller. The voltage controller is adjusted to increase or decrease the temperature setting of the oil bath. The oil bath-evaporator system (Make: Heidolph Instruments, Schwabach, Germany) shown in Fig. 3.4 was used in the present work. The set-up is available at Chemical Engineering Department, Thapar University, Patiala.

Fig. 3.4 Oil bath

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

This bath was used during the alkaline treatment of PET fibers at different temperatures. The maximum working temperature is adjustable upto 200 °C.

3.6.5 Vacuum Oven

The vacuum ovens are widely applicable for vacuum drying, baking, curing, and out-gassing solids and liquids. The vacuum oven (Make: Macro Scientific Works Pvt. Ltd., New Delhi, India) as shown in Fig. 3.5 was used in the present work. It is available at Chemical Engineering Department, Thapar University, Patiala. It is a microprocessor driven system implemented with high calibre temperature accuracy, uniformity and stability. The equipment is facilitated with convenient vacuuming, venting ports and easy to read vacuum gauge. The oven is provided with high quality door sealing made of silicone and highly safe viewing window made of tempered safety glass. In the present work, the oven was used for drying the nanoclay before its dispersion into the resin. It was also used for drying of PET fibers after their surface modification treatment in the alkaline solution. The oven was also used for degassing the epoxy-clay resin system to relieve any air entrapment during homogenizing process.

Fig. 3.5 Vacuum oven

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.6.6 Weighing Balance

The analytical weighing balance (Make: Mettler-Toledo, Greifensee, Switzerland) as shown in Fig. 3.6 was used for the experiments. It is available in Chemical Engineering Department, Thapar University, Patiala. The weighing balance has a high accuracy and precision, with a capacity of 320 g and a least count of 0.0001 g.

3.6.7 Universal testing machine

Universal testing machine (UTM) was used to determine the tensile strength, flexural modulus and flexural strength of the fabricated nanocomposites. UTM (Make: Zwick/Roell, Ulm, Germany) of 1 tonne (10 kN) capacity with different auxiliary attachments for tensile and flexural testing was used in the present work. This equipment is shown in Fig. 3.7 and is available at Chemical Engineering Department, Thapar University, Patiala.

Fig. 3.6 Weighing balance

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

Tensile testing samples were prepared as per the ASTM D3039/ D3039M which is a standard test method for determining tensile properties of polymer matrix composite materials. This test method determines the in-plane tensile properties of polymer matrix composite materials reinforced by high-modulus fibers. The sample size for tensile testing was 250 × 25 × 2.5 mm^3. Flexural testing or three point bend test samples were prepared as per the ASTM D790 standard. This test measures the flexural strength and flexural modulus of reinforced and unreinforced plastics. These calculations allow choosing materials that do not bend when supporting the loads required for application. These calculations relate to the stiffness of the material. The test uses a three point bend fixture to bend plastic test bars to acquire the data needed to make the calculations. The sample size for flexural testing was 125 × 12. 7 × 3.2 mm^3. The strain rate was adjusted to 2 mm/min for both tensile and flexural testing.

3.6.8 X-Ray Diffractometer

X-ray diffraction (XRD) is a non-destructive analytical technique which can yield the unique fingerprint of Bragg reflections associated with a crystal structure. In the preparation of a polymer/clay nanocomposite it is important to know the degree of intercalation/exfoliation and its effect on the nanocomposite properties. In other words, there is a need to analyze the microstructure of the prepared nanocomposite and to characterize the microstructure of nanocomposite as well as of pure/ organo-clay. Pure clay and organo-clay show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in the clay structure. Using the peak width at half maximum height and peak position (2θ) in the XRD spectra, the inter layer space can be calculated utilizing Bragg's law. The 2θ range is varied from 2–80 degree.

Fig. 3.7 Universal testing machine

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

X-ray diffractometer as shown in Fig. 3.8 (Make: X'Pert PRO, PANalytical, Almelo, Netherlands). The diffractometer is available at SAI Labs, Thapar Technology Campus, Patiala.

3.6.9 Scanning Electron Microscope

Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons that produce SEM images. Secondary electrons are most valuable for showing morphology and topography of samples. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Fig. 3.8 X-ray diffractometer

(Photo courtesy: SAI Labs, Thapar Technology Campus, Patiala)

SEM as shown in Fig. 3.9 **(**Make: JSM-6510LV, JEOL Ltd, Tokyo, Japan**).** It is a high-performance and low vacuum SEM for fast characterization and imaging of fine structures and has a magnification range from 5–300,000 X (printed as a 128 mm x 96 mm micrograph). The selectable “low vacuum” mode allows for observation of specimens that cannot be viewed at high vacuum due to excessive water content (like many biological samples) or because they have a non-conductive surface. The facility is available at *SAI Labs, Thapar Technology Campus, Patiala.* It was used to analyze the surface topology of the treated fibers.

3.7 Experimental Procedure

The experimental procedure contains the details about preparation of composites and alkaline treatment of fibers for various conditions.

Fig. 3.9 Scanning electron microscope

(Photo courtesy: SAI Labs, Thapar Technology Campus, Patiala)

3.7.1 Fabrication of Composites

The various steps involved in the processing and fabrication of nanocomposites in the present work are described as follows. The steps are:

1. The relative weight percent of constituents of the nanocomposite system (i.e. epoxy resin, clay, PET fibers and hardener) was calculated as follows:

   Calculate the weight of constituents by deciding the final weight of the composite. Let the final weight of the composite be 250 g.

   Example: For a composite containing 3% clay and 1% PET fibers by weight.

   Total weight of the composite = 250 g

   Weight of clay = 0.03×250 = 7.5 g

   Weight of PET fibers = 0.01 ×250 = 2.5 g

   Weight of the resin and hardener = 250- (2.5+7.5) = 240 g

   Weight of hardener = (35/135) × 240 = 62.22 g (as recommended by the supplier, the epoxy and hardener were mixed in the ratio 100:35)

   Weight of resin = 240- 62.22 = 177.78 g

2. Weigh 177.78 g of resin in a plastic beaker.
3. Add measured amount of clay to the resin. Make sure that the clay is dried for 2 hours at 80 ℃ in a hot air vacuum oven, before adding it to the resin.
4. Clay-resin mix is homogenized for 10 min, at 20,000 rpm using a homogenizer, as shown in Fig. 3.1.
5. The mix is sonicated for 10 min using probe sonicator, as shown in Fig. 3.2 (a).
6. Let the mix cool down before further processing (as its temperature gets raised upto 80 ℃ approximately).
7. Place the beaker in the vacuum oven, as shown in Fig. 3.5, for at least 20 min, and apply vacuum (760 mm Hg below atmospheric pressure) to remove entrapped air, if any.
8. In the meantime, arrange the mold to rest completely in a horizontal plane, using a spirit level and some packing, as shown in Fig. 3.10. This is required to obtain uniform thickness in the entire fabricated composite.

Fig. 3.10 Mould levelling using spirit level

9. Add the calculated amount of fibers to the resin system. Use the mechanical stirrer as shown in Fig. 3.3, at 350 rpm for 15 min, to disperse the fibers uniformly.
10. Add the calculated amount of hardener, and again use the mechanical stirrer at 300 rpm for 06 min to mix the hardener.
11. Coat the mold with the releasing agent (Frekote C-200, *Suppliers: Northen Composites*) with the help of a brush as shown in Fig. 3.11. The coating ensures easy removal of the fabricated

nanocomposite from the mold. The coating must be done at least 5 min prior to the pouring of the epoxy-clay-PET resin to the mold.

Fig. 3.11 Coating of mould with release agent

12. After mixing the hardener to the resin system, the mix is immediately poured into the aluminium mold, as shown in Fig. 3.12.

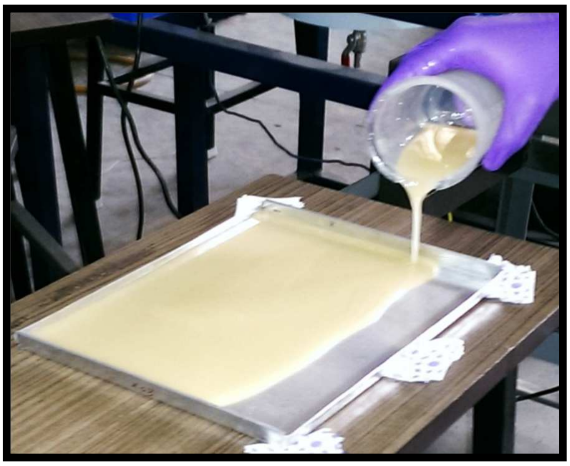


Fig. 3.12 Pouring mix in the mold

The following precautions can be taken:

1. Clay should be kept at elevated temperature (80 °C) for atleast 2 hours and before adding it to the resin, there should not be a large time gap between drying of clay and adding it to the resin, as it will again regain moisture from the environment.

2. While using the homogenizer, give an intermittent rest period, in order to avoid overheating.
3. Before adding hardener to the epoxy-clay-PET system, make sure that the mix is at ambient conditions (room temperature) or else the gel time will be achieved sooner than needed.

3.7.2 Surface Treatment of Fibers

The surface treatment of fibers was done in order to achieve rough surface on the fibers. The coarsening/ pitting can provide additional, mechanical bonding between the fibers and resin. The concentration of NaOH solution, treatment time and temperature of solution decides the degree of unevenness obtained.

The various steps involved in the surface treatment of fibers in the present work are described as follows. The steps are:

1. Prepare a 50 % concentrated NaOH solution (weight/volume), by adding NaOH pallets to the distilled water. Fig. 3.13 shows the NaOH pallets used in the present work.
   Example: For 50 g of NaOH pallets, take 100 mL of distilled water.

Fig. 3.13: NaOH pellets for preparing alkaline solution

2. Stir the pallets in distilled water thoroughly, using a glass spatula.
3. Adjust the oil bath at the temperature required for the specific condition.

4. Place the beaker in the oil bath using three prong clamp and adjustable stand, as shown in Fig. 3.14.

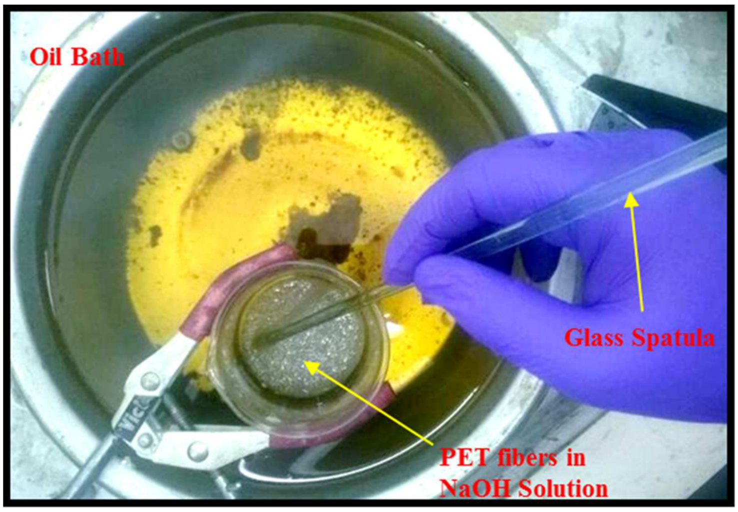


Fig. 3.14 Fibers dipped in NaOH solution in an oil bath

5. Dip the fibers to be treated, into the beaker, for the time decided, as shown in Fig. 3.14.
6. Keep on stirring the immersed fibers, intermittently.
7. As soon as the stipulated treatment time is over, pour all the fibers into the Buchner funnel, as shown in Fig. 3.15.

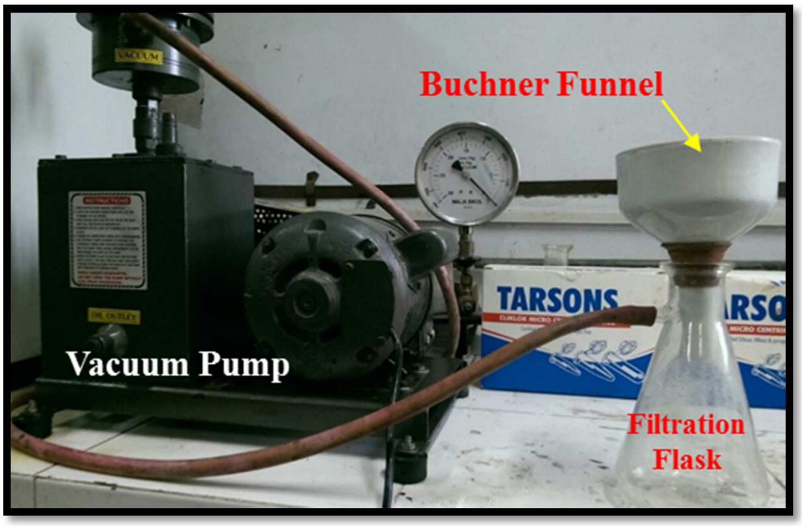


Fig. 3.15 Filtration set-up

8. Rinse the treated fibers thoroughly with distilled water.
9. Rinse the fibers for a suitable period of time with distilled water until all the sodium hydroxide is eliminated. This is confirmed by using litmus paper test for the water which rinsed the fibers (if the rinsed water does not contain any sodium hydroxide, the litmus paper remains red and does not change its color to blue).
10. Wrap the fibers in a filter paper and place them in oven under vacuum at 60 °C for 24 hours.

3.7.3 Sample Preparation

Specimens for tensile and flexural test were prepared using a circular saw. Tensile specimens were prepared as per ASTM 3039/3039M. The samples are shown in Fig. 3.16.

Fig. 3.16 Tensile testing specimens

Fig. 3.17 Flexural testing specimens

Specimens for flexural testing were prepared as per ASTM D790 and are shown in Fig. 3.17. Samples prepared for SEM images of treated PET fibers are shown in Fig. 3.16 (a) and samples for XRD were shown in Fig. 3.16 (b). XRD results will be used to find the extent of intercalation of epoxy in clay galleries during composite fabrication and the effect of amount of clay on the level of intercalation. The XRD samples were prepared in powder form using a blender.

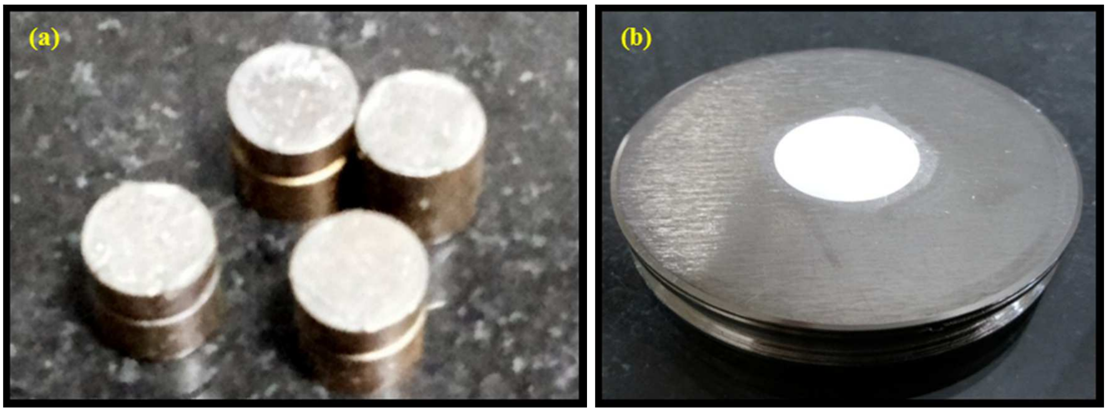


Fig. 3.18 (a) SEM specimens (b) XRD powder samples

3.8 Summary of the Chapter

This chapter puts forward the design of the present study. In this chapter of the report, the objective function with key issues has been discussed. An overview of the methodology, experimental procedure to be followed has also been described. The chapter also discusses about the machines and equipment which have been used during the fabrication and testing of fabricated composites. Finally, the chapter describes the procedure for sample preparation for tensile and flexural testing as well as the samples for SEM and XRD analysis.

Chapter 4

Results and Discussion

4.1 Introduction

The chapter brings forward the results obtained after fabrication and mechanical testing of the composites prepared as per mixture design table discussed in chapter 3. The experimental runs were conducted as per the run order and weight concentrations of constituents provided by the mixture design table (Table 3.1). The tensile and flexural properties for the given set of combinations were obtained and compared with the base matrix properties. SEM images of treated fibers for different time and temperature conditions as discussed in chapter 3, were obtained. The pitting and bending (morphology) of fibers was observed in order to select the time-temperature treatment conditions which showed potential to improve the properties. XRD for different combination of epoxy and clay system were obtained to diagnose the level of intercalation. Finally, nanocomposites with treated fibers were prepared for a selected composition and subsequently tested. These improvements have also been reported.

4.2 Base Material

The base material used in the present work was of an epoxy (GY 257) belonging to the Araldite family. The epoxy-hardener system was mixed in the ratio (100:35) as per the manufacturer recommendation The epoxy-hardener system was prepared using the standard procedure and the material was subjected to tensile and flexural testing on the UTS. The results of testing (tensile strength, bending strength and flexural modulus) were obtained and are shown in Table 4.1.

Table 4.1 Mechanical properties of the pure epoxy-hardener system

Tensile Strength (MPa)	Bending Strength (MPa)	Flexural Modulus (MPa)
37.5	96.2	3263.35

4.3 Nano-filler Dispersion in Resin System

X-ray diffraction analysis was conducted for the epoxy-clay samples (with no PET content) containing different nanoclay loadings. Diffraction analysis was performed to confirm the changes in d-spacing of clay when it was dispersed in the epoxy. Literature reports that d-spacing of pristine clay should increase when properly dispersed in the resin (Liu et al., 2004; Gupta et al., 2007). Thus, XRD results were required to check if the processing steps (and process parameters) followed during the fabrication process were effective in dispersing the clay in the resin system.

The d-spacing and Bragg`s angle values observed for different samples are presented in Table 4.2. The diffraction peak of pristine clay (Closite 15A) clay was observed at an angle of (2θ) 4.4216° having a d-spacing value of 19.96 Å. From the table it is observed that as the 2θ angle corresponding to the peak decreases, it is accompanied with an increase in the d-spacing value for the clay. It was inferred from the XRD results that d-spacing of clay increased from 19.96 Å to a higher range of 29.2–30.0 Å with addition of clay to the polymer system. This indicated that the processing method was correct as epoxy chains were intercalated into the nano clay layers due to polymerization of epoxy between clay layers. Some selected XRD graphs are presented in Fig. 4.1 (a–b). The details of XRD results are presented in Appendix I.

Table 4.2 d-spacing of clay layers in the epoxy clay nanocomposites

S. No.	Epoxy-clay system with clay loading (wt. %)	Angle (2θ)	d-spacing (Å)
1	100 (Pure/ Pristine Clay)	4.4216	19.96
2	0.75	3.0059	29.3
3	1.5	2.9384	30.0
4	2.25	2.9894	29.5
5	3.0	3.0221	29.2

4.4 Results of Mechanical Testing

Table 4.2 presents the tensile strength, bending strength, and flexural modulus values obtained from UTM testing for the 9 distinct compositions obtained by Mixtures Design (DOE, Minitab 17). A total of 18 runs (nine runs replicated twice) are presented in the table. For each run, four specimens were tested under bending and tensile testing.

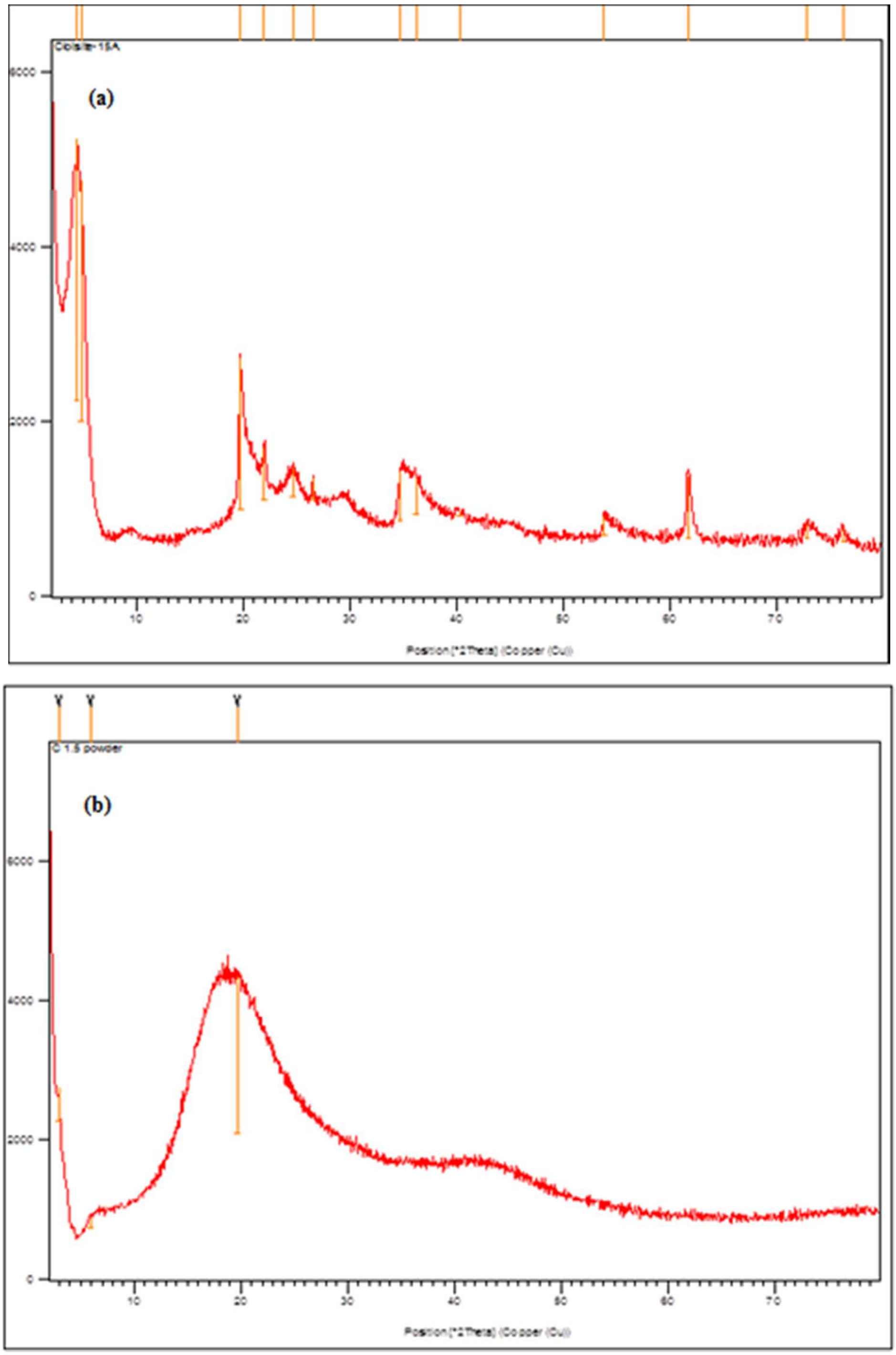


Fig. 4.1 XRD graphs for a) Pristine clay b) composite with 1.5 wt. % clay

Table 4.3 Results of testing obtained from UTM

Run Order	Epoxy-Hardener System (%)	Clay (%)	PET (%)	Tensile Strength (MPa)	Bending Strength (MPa)	Flexural Modulus (MPa)
1	97.1875	1.6875	1.125	27.8	51.3	2763.3
2	98.1250	1.1250	0.750	33.1	60.7	2796.7
3	96.2500	2.2500	1.500	26.7	56.0	2473.3
4	98.3125	0.5625	1.125	39.5	67.0	2796.7
5	98.5000	0.0000	1.500	41.9	64.0	2830.0
6	100.000	0.0000	0.000	36.5	93.7	3196.7
7	97.7500	2.2500	0.000	34.9	83.3	3500.0
8	97.1875	1.6875	1.125	34.3	53.0	2870.0
9	98.5000	0.0000	1.500	43.3	67.0	2860.0
10	98.1250	1.1250	0.750	36.9	64.0	2840.0
11	99.0625	0.5625	0.375	40.7	66.0	2680.0
12	97.9375	1.6875	0.375	36.4	60.0	2710.0
13	99.0625	0.5625	0.375	40.7	66.0	2680.0
14	96.2500	2.2500	1.500	27.6	57.0	2530.0
15	97.7500	2.2500	0.000	38.6	85.0	3580.0
16	100.000	0.0000	0.000	38.7	99.0	3330.0
17	97.9375	1.6875	0.375	36.4	60.0	2710.0
18	98.3125	0.5625	1.125	41.4	68.0	2900.0

4.4.1 Regression Analysis

Regression analysis was used in the present study to analyze relationships among various concentrations of constituents (epoxy, PET and clay) and the resulting response variables (tensile strength, bending strength and flexural modulus). The analysis was carried out through an estimation of a relationship between variables and responses. The results of this analysis served the purpose of calculating the extent of change in an observed response variable for changes in the ratio of constituents and also for predicting the response values for any given composite composition. The results of this analysis are shown in Appendix II–IV.

For the present work, a full cubic regression model was used to make the predictions. The model was fitted using Minitab 17 following the steps: Stat > DOE > Mixture >Analyze Mixture Design > Terms > Full Cubic. The model fitted well and obtained the adjusted R-squared values of 81.51, 94.09, 94.41 % for tensile strength, bending strength and flexural modulus respectively.

4.4.2 Tensile Strength of Composite System

This section describes the changes observed in the tensile strength of the nanocomposite system with changes in composition. For the obtained results, a regression analysis was conducted (Appendix II). The maximum improvement in tensile properties was observed for epoxy-PET fiber blend containing maximum weight percentage of PET (1.5 wt. %). The maximum tensile strength was recorded as 41.9 MPa (1.5 % PET, and 0 % clay). Thus, the maximum improvement obtained in tensile strength was nearly upto 12 % over that of the base material. It may be noted here, that nanocomposites containing both PET and clay in their higher ranges, deteriorated the tensile properties considerably. PET fibers are considered as ductile thermoplastics which helped in upgrading the tensile properties. Further, it may be noted that presence of clay, even at the maximum weight percentage (2.25 wt. %) did not deteriorate the tensile properties significantly. This shows that nano-filler has be used in the correct maximum range, not causing any agglomeration (when used as the only filler).

The following graphs describe the changes observed in the tensile strength of the nanocomposite system with changes in composition.

A. Mixture Contour Plot for Tensile Strength

The mixture contour plot shown in Fig. 4.2 describes the relation of the response variable (tensile strength) to the three constituents of the nanocomposite system. For any given composition in the design space, this contour plot can be used to obtain the value of response variable i.e. tensile strength. It can be observed that with increase in PET concentration in the nanocomposite for the same clay content, the tensile strength increases. For example, for nanocomposite system containing maximum PET (1.5 wt. %) with no clay, maximum tensile strength (41.9 MPa) has been achieved. With increase in clay content (from 0.5625 to 1.6875 wt. %), for the same concentration of PET (1.125 wt. %), tensile strength has decreased (39.5 to 34.3 MPa). However, it may be noted here that when the micro-filler and nano-filler are present at their higher ranges simultaneously in the nanocomposite system, the tensile strength decreases considerably. For example for nanocomposite constitutions (clay: 1.6875 wt. %, PET: 1.125 wt. %) and (clay: 2.25 wt. %, PET: 1.5 wt. %)where micro and nano-fillers both are present in a significant amount, the tensile strength dropped to lower values of 34.3 MPa and 27.6 MPa respectively. This shows that the epoxy-hardener system cannot accommodate both the fillers simultaneously in large amounts.

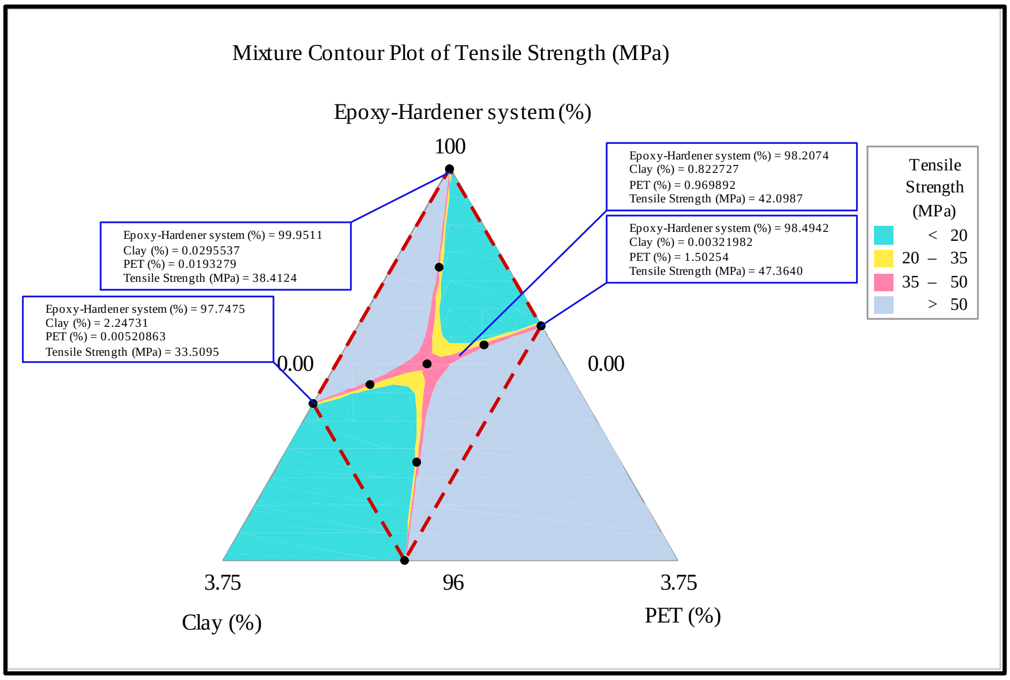


Fig. 4.2 Mixture contour plot for tensile strength

B. Mixture Surface Plot for Tensile Strength

A surface plot shows how a response variable (here, tensile strength) relates to three components based on a regression model. The mixture surface plot shows the effect of change in concentration of constituents (epoxy, clay, and PET) on the tensile strength of the fabricated nanocomposite. For the given data, the mixture surface plot shows that tensile strength is highest when PET is maximum. Also, the plot shows that if the clay is increased beyond the designed upper limit of 2.25 wt. %, tensile strength falls considerably. Also, the plot elaborates that if the fillers are present simultaneously in their upper range concentrations (2.25 wt. % clay, 1.5 wt. % PET, 96.25 wt. % epoxy), the epoxy does not accommodate them well and the tensile strength drops considerably. To maximize the tensile strength, choose proportions for the components in the upper right corner of the plot.

C. Cox Response Trace Plot for Tensile Strength

A response trace plot (also called a component effects plot) shows how each component affects the response relative to a reference blend. For the present work, the reference blend was given as (epoxy: 98.12, clay: 1.13, PET: 0.75; all in wt. %; obtained as the center point of the design space in Fig. 4.2) in composition. The Cox Response Trace Plot shown in Fig. 4.4 shows effect of each component on the tensile strength.

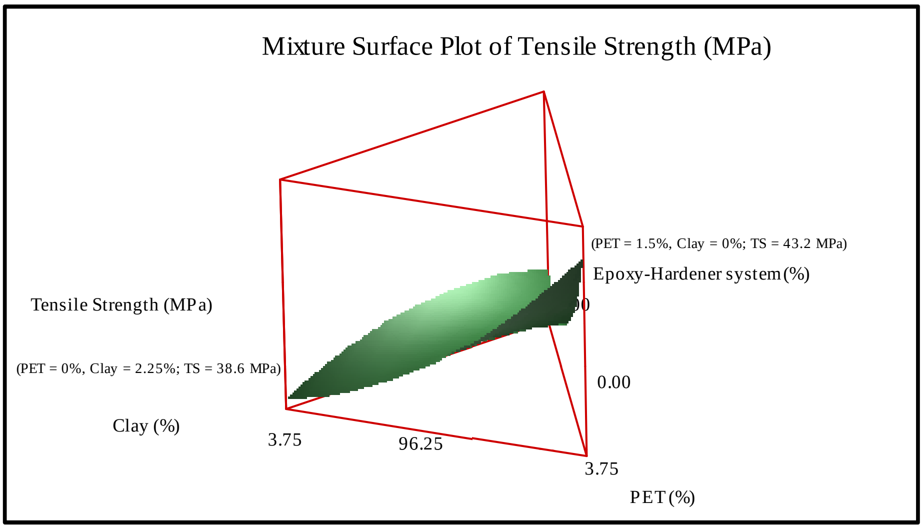


Fig. 4.3 Surface plot for tensile strength

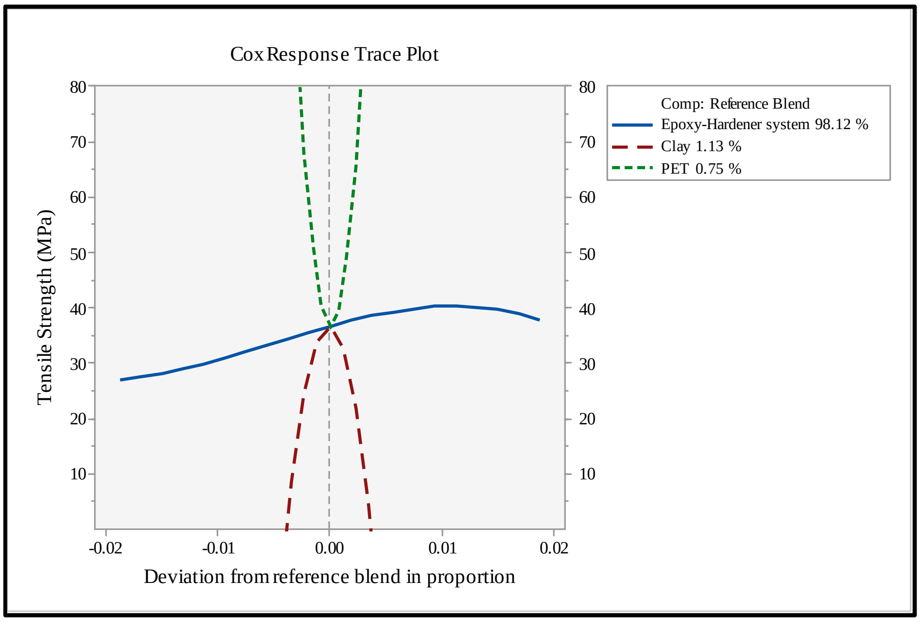


Fig. 4.4 Cox response trace plot for tensile strength

The trace plot provides information about the component effects. Starting at the location corresponding to the reference blend, the plot shows that as the proportion of epoxy in the mixture increases and the other mixture components i.e. clay and PET decrease, the tensile strength increases. Thus, the Cox plot concludes that if the nanocomposite is to contain the micro and nano fillers simultaneously, their combined wt. % should not refer to the sum of their higher ranges. Further, the plot illustrates that if the PET amount is increased beyond its concentration in the reference blend (i.e. decreasing the amount of epoxy and clay as compared to their amounts in the reference blend), the tensile strength increases and vice-versa. Similarly, the plot illustrates the effect of clay on the tensile properties, however showing a trend opposite of what was shown by PET addition. Thus, Cox plot concludes that with respect to the reference blend, if the PET concentration is increased or the clay concentration is decreased, the tensile strength increases.

4.4.3 Bending Strength of Composite System

This section describes the changes observed in the bending strength of the nanocomposite system with changes in composition. For the obtained results, a regression analysis was conducted (Appendix III). The bending strength for the neat epoxy-hardener system was observed to be 93.1 MPa. Addition of fillers (either clay, or PET or both) lowered the bending strength with reference to that of the neat epoxy-hardener system. The maximum bending strength observed for the nanocomposite system was 83.3 MPa. This value was obtained for composition with maximum clay content and no PET (2.25 wt. % clay and 0 wt. % PET). The minimum bending strength of 53 MPa was observed for 1.6875 wt. % clay and 1.125 wt. % PET. As was the case with tensile strength, for bending strength also, it was observed that when both the fillers were present in the nanocomposite system and that too their higher ranges, the bending strength values dropped drastically. For example, for total filler content of (2.25 wt. % clay, 1.5 wt. % PET), the bending strength was observed to be very low i.e. 57 MPa. This showed that there is some upper limit of the total micro and nano filler content which the nanocomposite system can accommodate.

A. Mixture Contour Plot for Bending Strength

The mixture contour plot shown in Fig. 4.5 describes the relation of the response variable (bending strength) to the three constituents of the nanocomposite system. It can be observed that maximum bending strength was observed for neat epoxy-hardener system i.e. 93.7 MPa. Also, the maximum bending strength obtained for the blend was 83.3 MPa which is at maximum concentration of clay (2.25 wt. % clay and 0 wt. % PET).

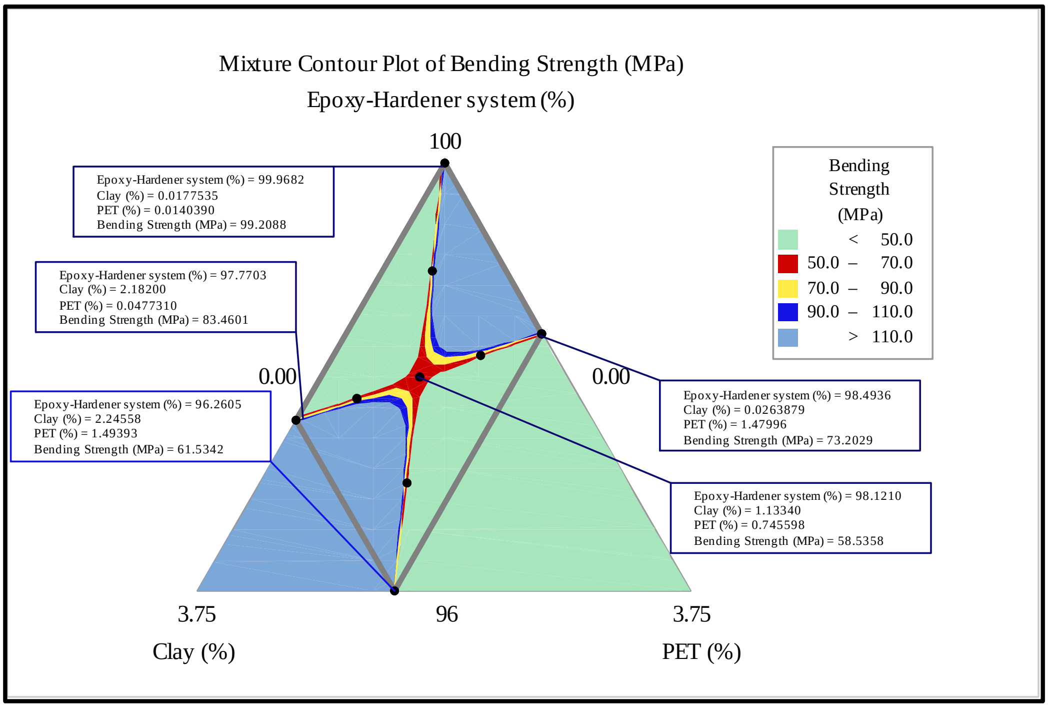


Fig. 4.5 Mixture contour plot for bending strength

Further on addition of only PET fibers (0 wt. % clay, 1.5 wt. % PET) to the base material, bending strength reduced to 67 MPa. These results show that addition of only clay component deteriorate the bending strength lesser as compared to addition of only PET fibers. The minimum bending strength was obtained at compositions of (1.6875 % clay, 1.125 wt. % PET) and (2.25 % clay, 1.5 % PET) as 53 MPa and 57 MPa respectively. Thus, the mixture contour plot recognized the regions (shown in flags) of poor bending strength and again confirmed them to be for compositions containing both micro and nano fillers simultaneously in their upper ranges, the nanocomposite system.

B. Mixture Surface Plot for Bending Strength

The mixture surface plot is showing the relation between the response variable (here, bending strength) and the various constituents, based on the regression analysis. The mixture surface plot shows the effect of change in concentration of constituents (epoxy, clay, and PET) on the bending strength of the fabricated nanocomposite. For the given data, the mixture surface plot shows that bending strength is highest for the pure epoxy-hardener system i.e. no addition of clay and PET. The surface plot illustrates that with increase in clay content in the nanocomposite system (with no PET addition), the bending has decreased but marginally (for maximum clay content of 2.25 wt. %). However, the plot shows that when PET amount is increased (in absence of clay), the bending strength decreased drastically. Further, the simultaneous addition of micro and nano filler (in any amount), has resulted in deterioration of the bending strength. The plot also shows that if both micro and nano fillers have to be added in the nanocomposite system for some special requirements, the top left corner of the plot should be targeted to obtained the desired concentration of constituents.

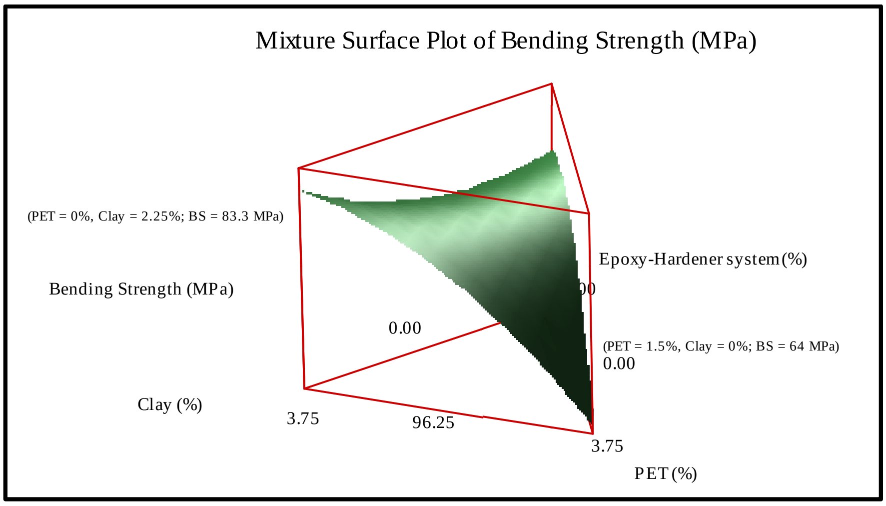


Fig. 4.6 Mixture surface plot for bending strength

C. Cox Response Trace Plot for Bending Strength

A response trace plot (also known as component effects plot) shows how each component affects the response (i.e. bending strength) with respect to a reference blend. For the present work, the reference blend was given of composition (1.13 wt. % clay and 0.75 wt. % PET). This composition corresponds to the center point of the design space in Fig. 4.5. The Cox Response Trace Plot shown in Fig. 4.7 shows the effect of each component on the bending strength.

The Cox response trace plot shown in Fig. 4.7 provides information about the component effects on the bending strength. Starting with the composition corresponding to the reference blend, the plot shows that as the proportion of epoxy in the mixture increases (and the other mixture components i.e. clay and PET decrease), the bending strength increases. The plot shows that any increase in the epoxy amount beyond the reference blend composition, results in a sharp increase in the bending strength values.

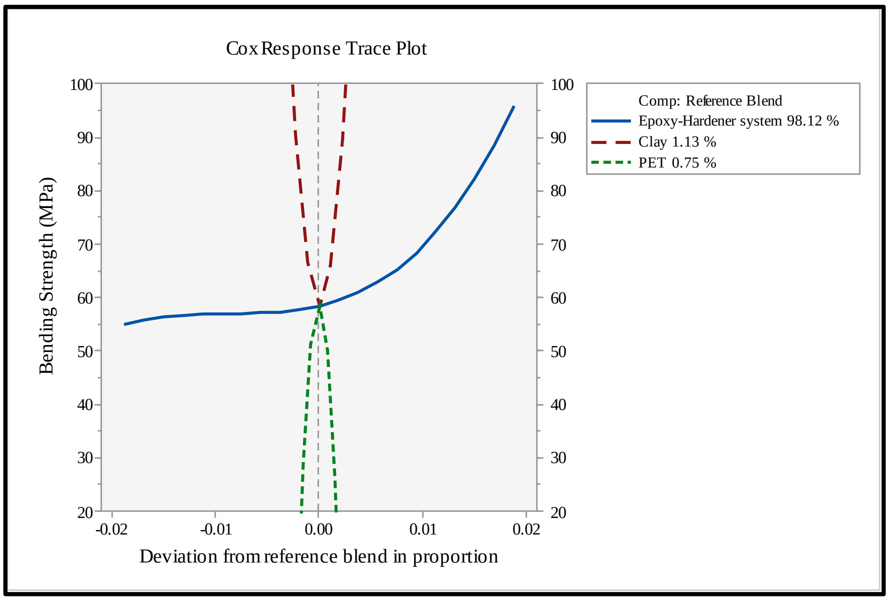


Fig. 4.7 Cox response trace plot for bending strength

This is supported by the results in Table 4.2 which show that maximum bending strength has been obtained for the neat epoxy-hardener system. The Cox plot clearly shows that when the epoxy content is at its minimum ranges (and thereby clay and PET are present in their combined higher proportions) in the nanocomposite, the bending strength is minimum. This again illustrates that addition of any filler to the epoxy-hardener system deteriorates the bending strength. However, with compositions containing lesser epoxy than the reference blend composition, the decrease in bending strength values has not been very drastic. This is because for all such compositions (containing lesser epoxy than the reference blend), the concentration of clay in the nanocomposite is always more than that of PET. It can be observed from Table 4.2 that addition of clay though deteriorates the value of bending strength but is able to restore it near the value obtained with neat epoxy-hardener system. Thus, in blends with lesser epoxy than the reference blend, because of dominance of the clay concentration over the PET concentration, the bending strength values have decreased but not significantly.

4.4.4 Flexural Modulus for Composite System

This section describes the changes observed in the flexural modulus of the nanocomposite system with changes in composition. For the obtained results, a regression analysis was conducted (Appendix IV). The flexural modulus for the neat epoxy-hardener system was observed to be 3196.7 MPa. The maximum improvement in flexural modulus was observed for epoxy-clay blend containing maximum weight percentage of clay (2.25 wt. %). The maximum flexural modulus was recorded as 3500 MPa (0 % PET, and 2.25 % clay). Thus, the maximum improvement obtained in flexural modulus was about 10% over that of the base material. It may be noted here, that nanocomposites containing both PET and clay in their higher ranges, deteriorated the flexural modulus considerably.

The following graphs describe the changes observed in the flexural modulus of the nanocomposite system with changes in composition.

A. Mixture Contour Plot for Flexural Modulus

The mixture contour plot shown in Fig. 4.8 describes the relation of the response variable (flexural modulus) to the three constituents of the nanocomposite system. For any given composition of the nanocomposite system within the design space, the mixture contour plot can be used to obtain the resultant flexural modulus. The contour plot shows that with maximum clay content, the flexural modulus increases to maximum. For example, for the composition (2.25 wt. % clay, and 0 wt. % PET), the flexural modulus was highest at 3500 MPa. Also, with addition of only PET to the composite system, the flexural modulus decreased significantly. For example, for the composition (0 wt. % clay, and 1.5 wt. % PET), the flexural modulus was 2860 MPa. Further, the minimum flexural strength for the nanocomposite system was obtained at (clay: 2.25 wt. %, PET: 1.5 wt. %)

as 2530 MPa. This showed that the epoxy-hardener system cannot accommodate both the fillers simultaneously in their higher amounts.

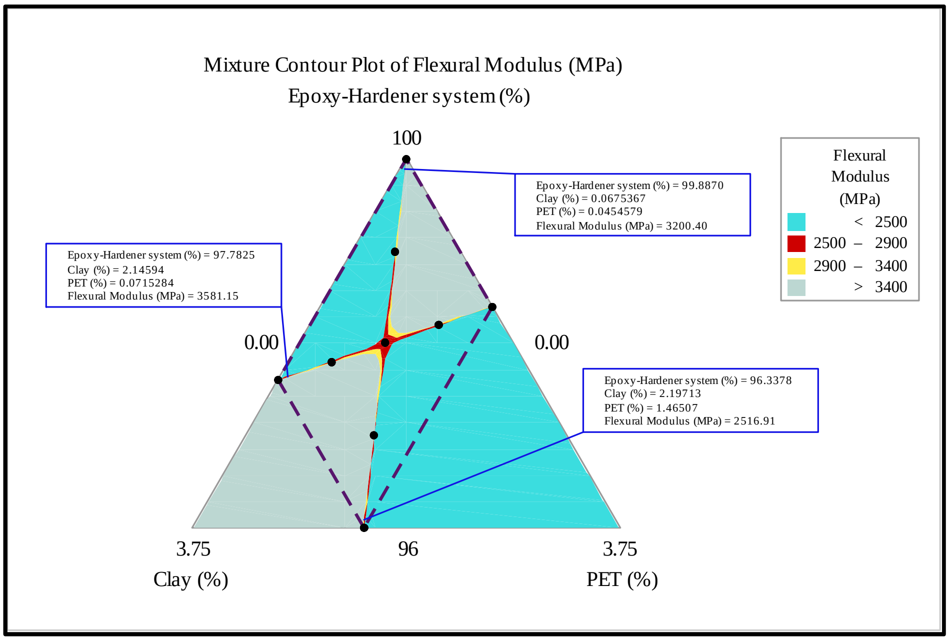


Fig. 4.8 Mixture contour plot for flexural modulus

B. Mixture Surface Plot for Flexural Modulus

A surface plot shows how a response variable (here, flexural modulus) relates to three components based on a regression model. The mixture surface plot shows the effect of change in concentration of constituents (epoxy, clay, and PET) on the flexural modulus of the fabricated nanocomposites.

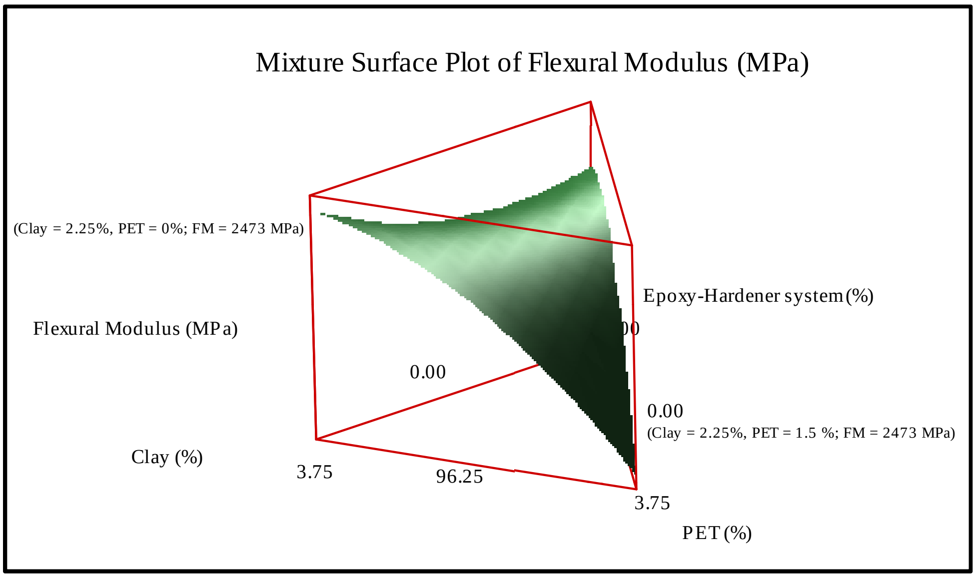


Fig. 4.9 Mixture surface plot of flexural modulus

For the given data, the mixture surface plot shows that flexural modulus is highest when clay is maximum (with no PET). Further, the plot elaborates that increase in PET concentration decreases the flexural modulus continuously. To maximize the flexural modulus, choose proportions for the components in the upper left corner of the plot.

C. Cox Response Trace Plot for Flexural Modulus

A response trace plot shows how each component affects the response relative to a reference blend. For the present work, the reference blend was given as (epoxy: 98.12, clay: 1.13, PET: 0.75; all in wt. %; obtained as the center point of the design space in Fig. 4.2) in composition. The Cox Response Trace Plot shown in Fig. 4.4 shows the effect of each component on the flexural modulus.

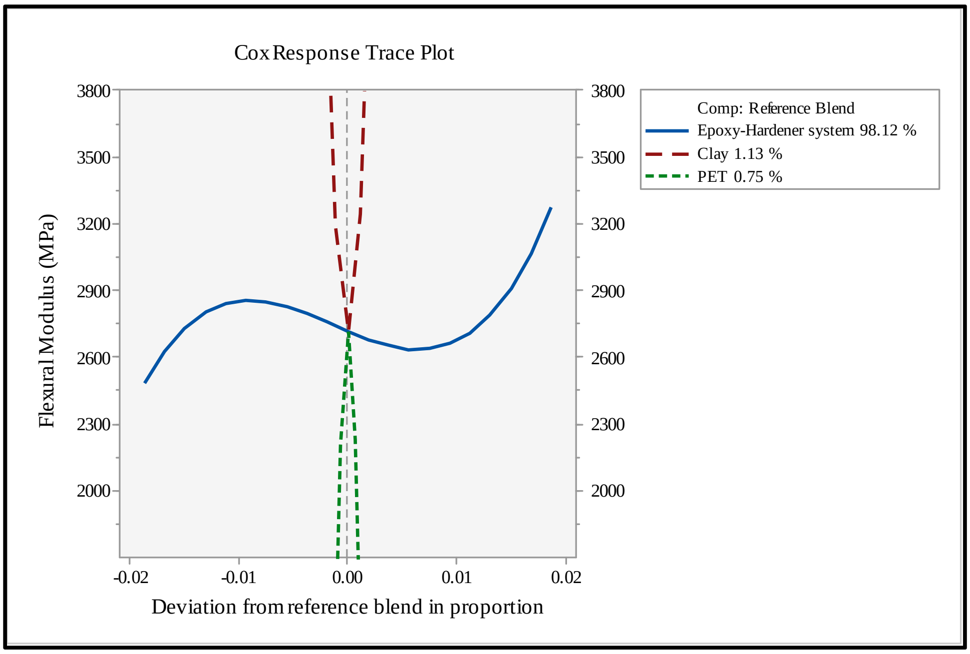


Fig 4.10 Cox Response Trace Plot for Flexural Strength

The trace plot provides information about the component effects. Starting with the region on to the left of the reference blend (i.e. nanocomposite compositions with less than 98.12 wt. % of epoxy), the plot shows a continuously changing trend with a minima and a maxima. The minima was obtained corresponding to the composition containing the fillers in their combined maximum amount (clay: 2.25 wt. %, PET: 1.5 wt. %, epoxy: 96.25 wt. %; flexural modulus: 2530 MPa). The maxima in this left blend region was obtained for nanocomposite system containing maximum clay with no PET (clay: 2.25 wt. %, PET: 0 wt. %, epoxy: 97.75 wt. %; flexural modulus: 3500 MPa). The reverse of this trend was shown in the right region (region on to the right of the reference blend). In the right region, the plot again showed a continuously changing trend with a minima and maxima.

4.5 Effect of Alkaline Treatment on Nanocomposite Properties

This section describes the various activities and results thereof listed under Phase II of the present experimental work. Here, initially the PET fibers were subjected to NaOH treatment under various temperature-time conditions. The treated fibers were then characterized using SEM analysis. Based on the topological changes on the surface of treated fibers and the recommendations of available literature, a few treatment conditions were selected. For these selected treatment conditions, nanocomposites for a given composition were fabricated with the treated fibers. These nanocomposites were subjected to mechanical testing to note the tensile and bending properties corresponding to different treatment conditions.

4.5.1 SEM Image Analysis

This section presents all the SEM images obtained for PET fibers treated under different temperature-time conditions. These images profoundly helped in selecting the treatment conditions for which the fibers (after treatment) on their additon to the composite system will favour an increase in tensile and bending properties of the composite.

Figure 4.11 (a–d) shows the SEM images for the treatment temperature of 31 ℃(room temperature) with treatment time periods of 2.5, 5, 10, 15 minutes respectively. The areas of modification by NaOH on the surface are seen like minute pores as seen in Fig. 4.11 (d). SEM images show that surface has not been modified adequately (not sufficiently rough) to provide any increased adhesion of PET to the resin.

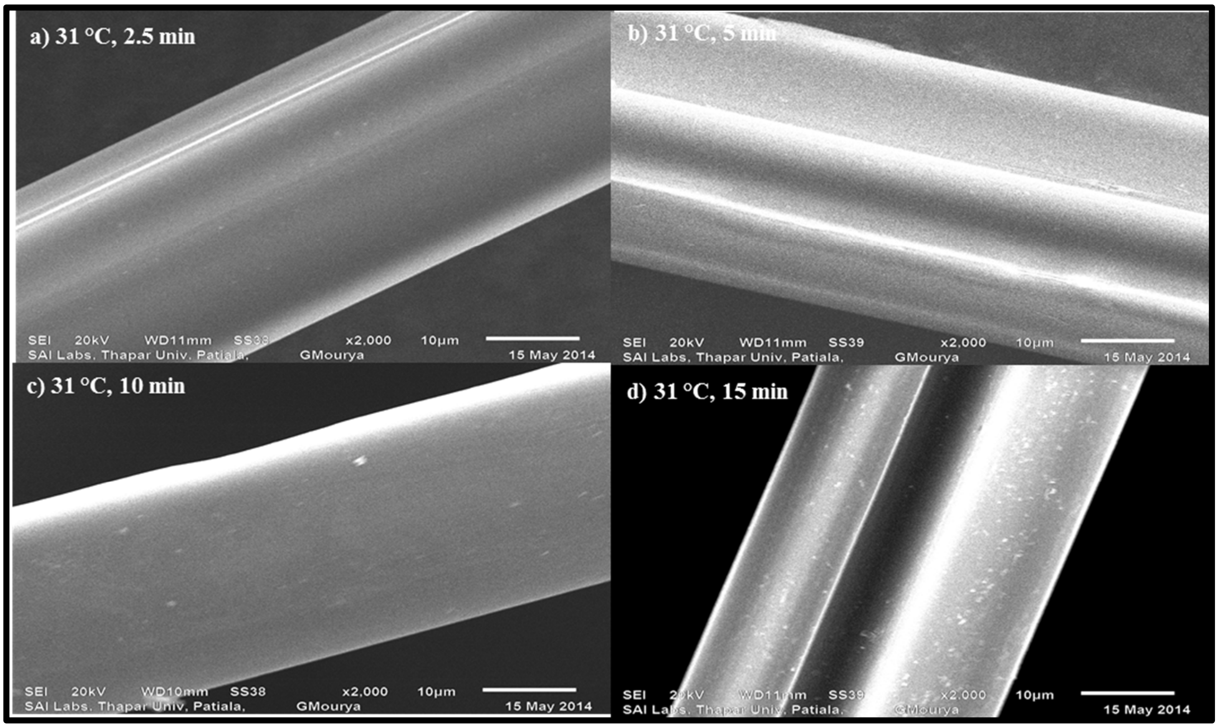


Fig. 4.11 SEM images of treated PET fibers for a) 31 ℃, 2.5 min b) 31 ℃, 5 min c) 31 ℃, 10 min d) 31 ℃, 15 min

Figure 4.12 (a–d) shows the SEM images for the PET fibers treated at a temperature of 50 ℃ (less than the glass transition temperature [69 ℃] of PET fibers) for time periods of 2.5, 5, 10, 15 minutes respectively. Images for soaking periods of 2.5, 5 and 10 minutes respectively did not show any significant changes on the surface of fibers. However, SEM image for 15 minutes of treatment time showed disfigurement, but which was not uniform over the entire surface of the fibers. The surface topology was still not even close to the required topology as reported by Teh et al. (2005).

Figure 4.13 (a–d) shows the SEM images for the treatment temperature of 80 ℃ with treatment time periods of 2.5, 5, 10, 15 minutes respectively. The treatment tempertaure considered here was above the glass transition temperature of PET fibers and thus a noticable change in surface topology of fibers was observed. The fibers treated for 2.5 and 5 minutes did not show any kind of pitting etc. but delusturing of the fibers could be noticed. The fibers treated for 10 and 15 minutes respectively showed significant amount of pitting.

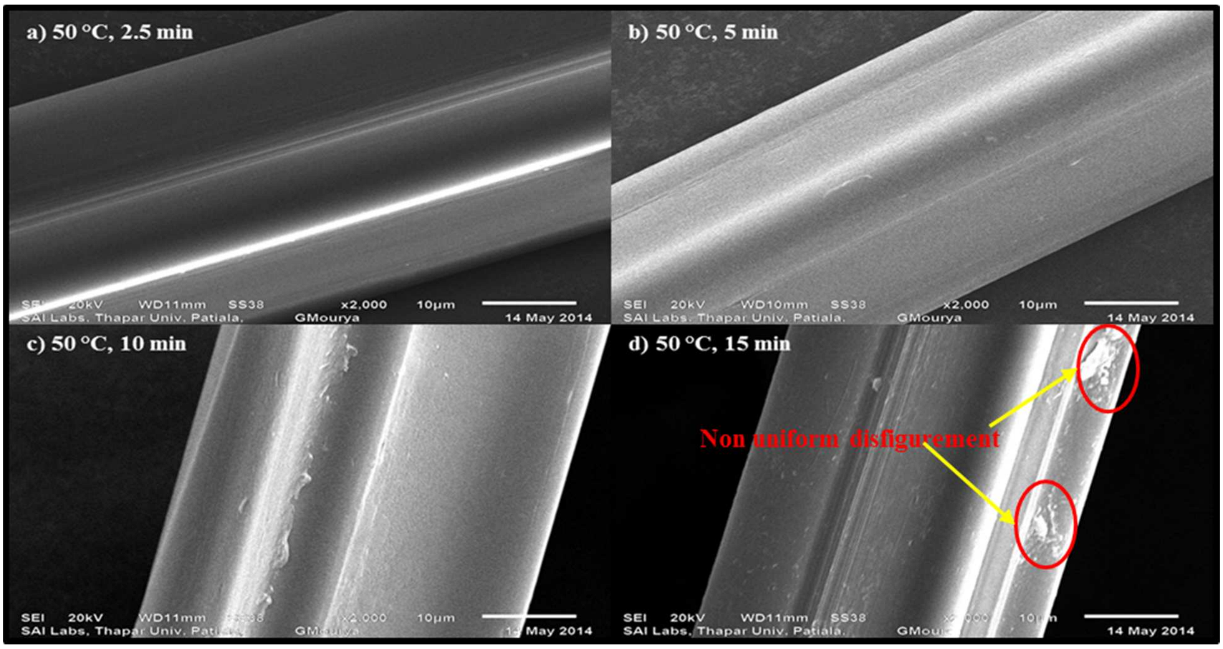


Fig. 4.12 SEM images of treated PET fibers for a) 50 ℃, 2.5 min b) 50 ℃, 5 min c) 50 ℃, 10 min d) 50 ℃, 15 min

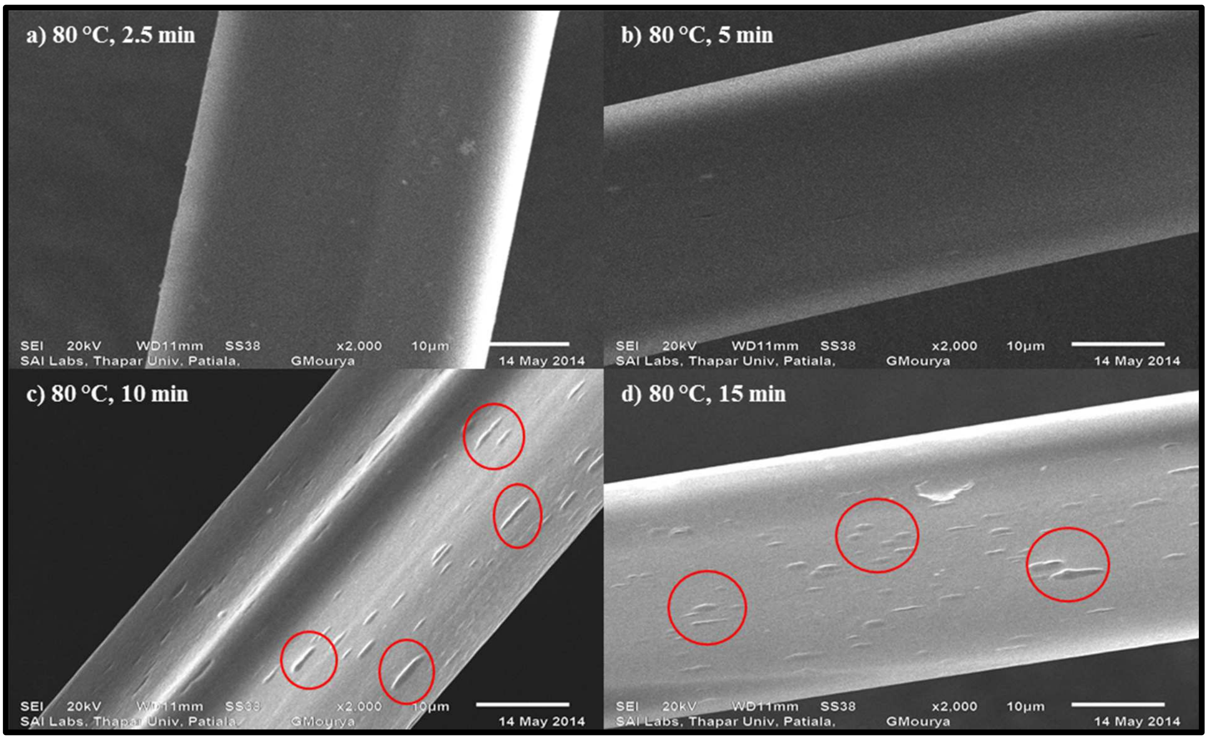


Fig. 4.13 SEM images of treated PET fibers for a) 80 ℃, 2.5 min b) 80 ℃, 5 min c) 80 ℃, 10 min d) 80 ℃, 15 min

This kind of morphology was required as per the reported literature for fullfilling the objective of the study. However, PET fibers were still subjected to more severe treatment conditions. They were subjected to NaOH treatment at 80 ℃ for prolonged periods of 30 min and 45 min respectively. Figures 4.14 and 4.15 show the surface details of the treated fibers for treatment conditions of 30 min and 45 min respectively for treatment at 80 ℃. For these large time periods, another characteristic observed was excessive bending of the fibers during the course of treatment along with scaling-off of the edges of fibers, as shown in Fig. 4.14 (b) and Fig. 4.15 respectively. The areas of attack by the alkaline solution on the fiber surface were observed as small craters/ pores etc. However, under extremely severe conditions of treatment (80 ℃ for 30 min and 45 min respectively), surface gets deteriorated because of coalescence of several craters/ pores etc. at particular locations as shown in Fig. 4.15.

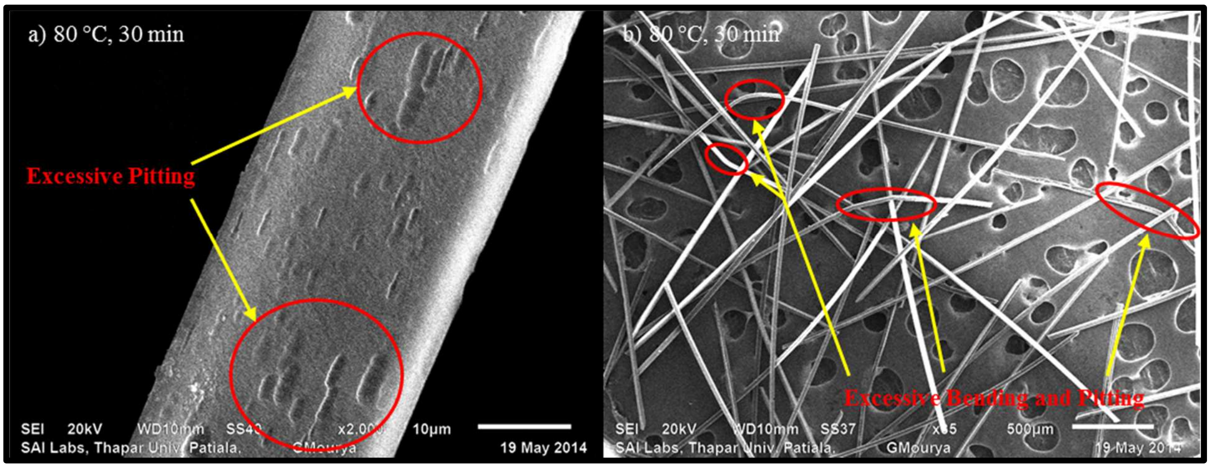


Fig. 4.14 SEM images of treated PET fibers for a) 80 ℃, 30 min (2000X) b) 80 ℃, 30 min (35X)

4.5.2 Property Evaluation of Nanocomposite with Treated Fibers

From the SEM analysis conducted on treated fibers in section 4.6.1, four treatment conditions were considered appropriate to be having potential to improve the mechanical properties of the nanocomposite. The selected temperature-time conditions for alkaline treatment were at 80 ℃ with treatment time of 2.5, 5, 10 and 15 min respectively.

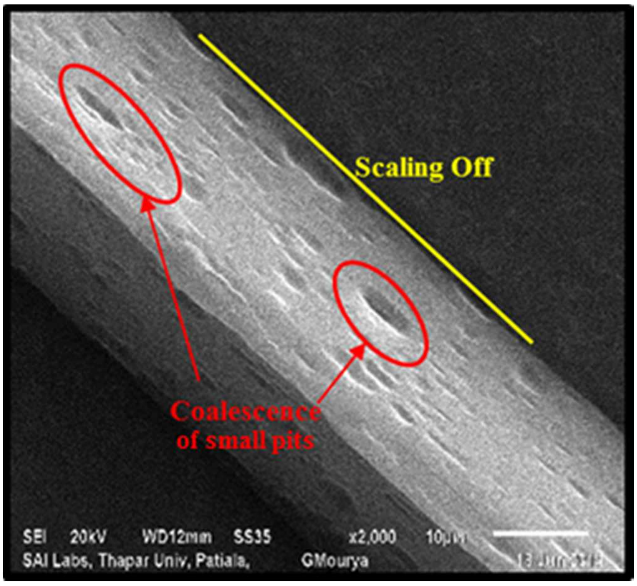


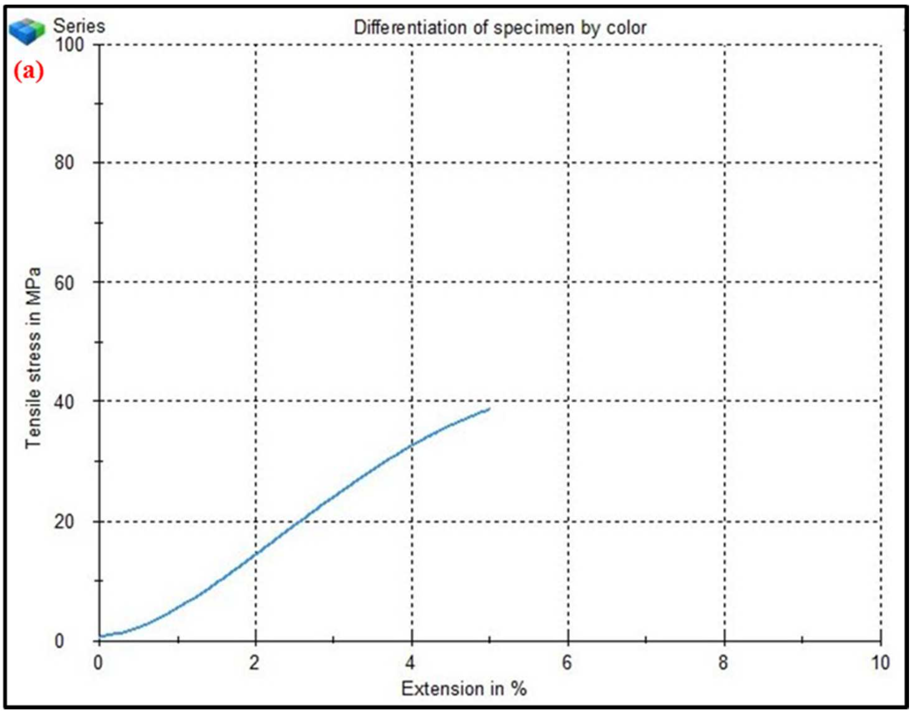
Fig. 4.15 SEM images of treated PET fibers for 80 ℃, 45 min

For this, nanocomposites for the above selected conditions were again fabricated according to the steps described in Chapter 3 (Section 3.7.1). The composition selected for testing was (clay: 0.8

wt. %, PET: 1.00 wt. %, epoxy-hardener: balance). The results of mechanical testing for nanocomposites with untreated and treated fibers are shown in Tables 4.3–4.4.

Table 4.3 shows the results of tensile testing. It can be observed from the table that treatment conditions of 2.5 and 5.0 min at 80 °C have not resulted in increase in the tensile strength as compared to value obtained with untreated fibers. For treatment time of 10 min, a slight improvement in tensile strength has been observed. However, the best results were obtained for treatment conditions of 80 °C with 15 min of treatment time. The stress vs. extension curves for tensile testing under some selected conditions are shown in Fig. 4.16 (a–c).

The experimental work conducted in Phase I had shown that on adding PET fibers to the epoxy-clay nanocomposite system had mainly improved the tensile strength. Further, in Phase II of work (as discussed above), it was observed that maximum improvement in tensile strength was achieved by alkaline treatment of the fibers under the conditions (80 °C, 15 min). Thus, for this treatment condition, the nanocomposite was tested under bending to compare the results of bending strength and flexural modulus with those of the nanocomposite with untreated PET fibers. The flexural stress vs. defection curves for flexural testing under both the conditions (untreated fibers; fibers treated for 15 min at 80°C) are shown in Fig. 4.17 (a–b).



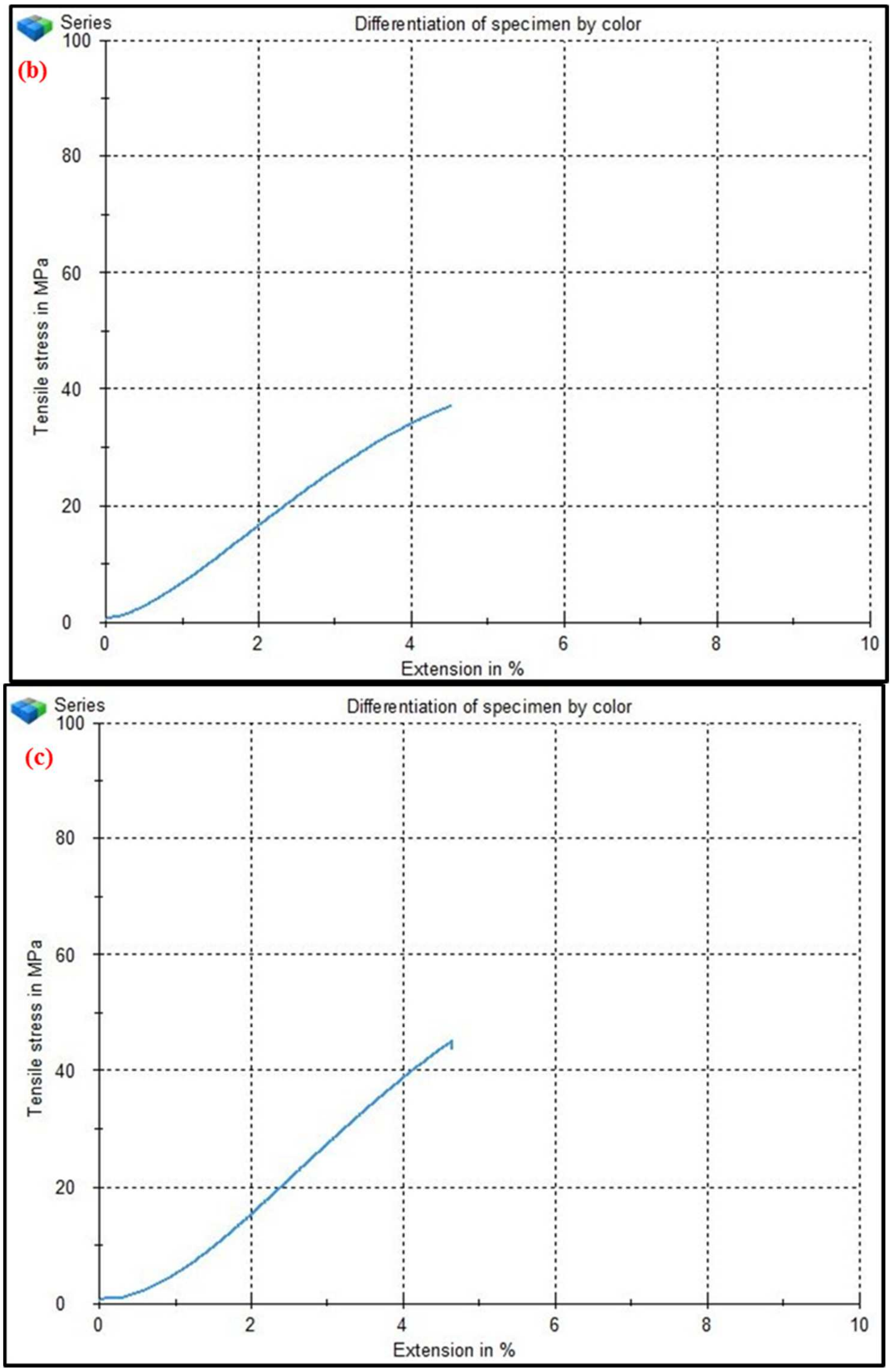


Fig. 4. 16 Tensile stress vs. extension curve for 0.8 wt. % clay and 1 wt. % PET (a) untreated (b) 80 ℃, 2.5 min (c) 80 ℃, 15 min

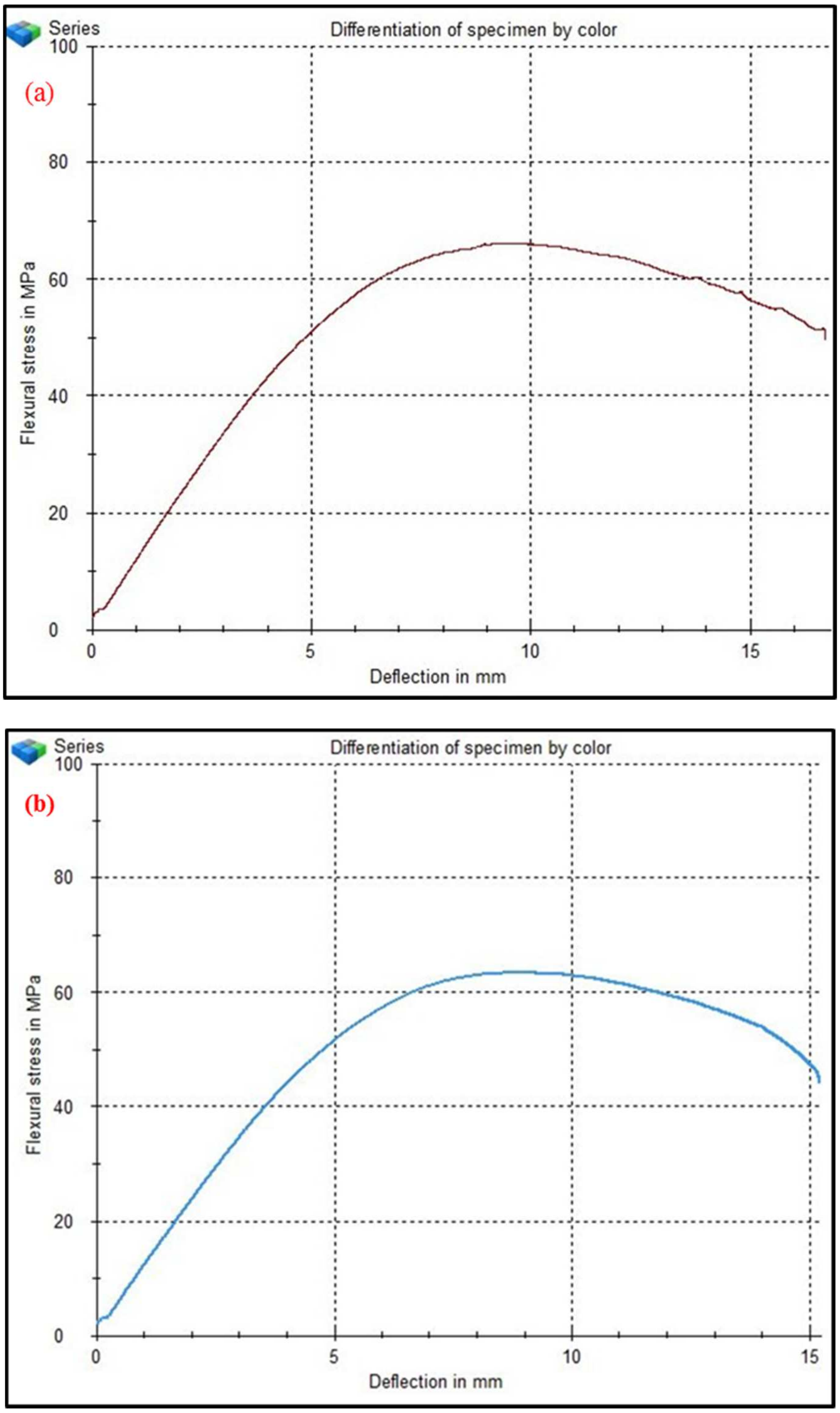


Fig. 4. 17 Flexural stress vs. deflection curve for 0.8 wt. % clay and 1 wt. % PET (a) untreated (b) 80 ℃, 15 min

Table 4.4 Tensile testing results for nanocomposite with treated fibers

Nanocomposite composition: 0.8 wt. %, 1.0 wt. % PET, epoxy-hardener: balance Treatment temperature: 80 ℃					
Treatment time (min)	0*	2.5	5	10	15
Tensile strength (MPa)	38.7	38.5	38.6	40.7	44.5

* Untreated PET fibers in the as-received form

Table 4.5 Flexural testing results for nanocomposite with treated fibers

Nanocomposite composition: 0.8 wt. %, 1.0 wt. % PET, epoxy-hardener: balance Treatment temperature: 80 ℃		
Treatment time (min)	0*	15
Bending strength (MPa)	66.25	65.5
Flexural modulus (MPa)	2277.5	1943.333

* Untreated PET fibers in the as-received form

The results show that the treatment of PET fibers under the selected time-temperature conditions resulted in slight reduction in the nanocomposite’s properties under flexural testing. However, since the decrease is not drastic whereas the increase in tensile properties achieved through the selected treatment conditions was significant, the said conditions are useful in improving the overall properties of the nanocomposite system through addition of treated PET fibers.

Chapter 5

Conclusions

5.1 Introduction

The chapter brings forward the conclusions drawn from the present experimental work. It also discusses the major inferences and recommendations and the scope of future work.

5.2 Results and Conclusions

Fabrication of Nanocomposites

- Fabrication of nanocomposites involves a definite sequence of processing steps which have to be adhered to carefully. Before mixing the constituents, the fillers (PET, and clay) have to be dried for sufficient periods of time in order to get rid of moisture. Initially, the clay is added to the epoxy and is dispersed using a homogenizer (20,000 rpm) and a probe sonicator. This is followed by addition of PET fibers dispersed using a mechanical stirrer. After the fibers are homogeneously dispersed, the hardener is added and again mechanical stirrer is used to mix the constituents. After addition of hardener, mixing is done for upto 5–7 minutes. Finally the mix (blend) is poured into an aluminium mould coated with a releasing agent.

XRD Analysis

- The d-spacing of pristine clay (Closite 15A) is observed to be 19.96 Å.
- It is inferred from the XRD results that d-spacing of clay has increased from 19.96 Å to a higher range of 29.2–30.0 Å on addition of clay to the polymer system. This indicates that the processing method is correct as epoxy chains have intercalated into the nano clay layers due to polymerization of epoxy between clay layers.
- Also, the increasing amount of clay in the resin has not made any considerable changes in the extent of intercalation, thus concluding that the range in which clay has been varied is correct and acceptable.

Tensile Property

- The tensile strength recorded for neat epoxy-hardener system (no fillers) is 38.7 MPa.
- The maximum improvement in tensile properties (UTS≈42 MPa) has been observed for epoxy-PET fiber blend containing maximum weight percentage of PET (1.5 wt. %) with no clay content. The maximum improvement obtained in tensile strength was upto 12% over that of the base material. Thus, it was concluded that addition of only PET fibers improved the tensile strength. PET fibers are considered as ductile thermoplastics which help in upgrading the tensile properties (Teh *et al*., 2005).
- With increase in clay content (from 0.5625 to 1.6875 wt. %), for the same concentration of PET (1.125 wt. %), tensile strength has decreased (39.5 to 34.3 MPa). This change witnesses that increase in clay content decrease the tensile strength. The decrease in tensile strength values, could be explained by the stress concentration effect of agglomerated clay particles at higher clay loadings leading to lowering of filler surface area and thus lower polymer/clay surface interaction (Isik *et al.*, 2003; Azeez *et al.*, 2013; Kusmono *et al.*, 2013).
- The results reveal that when micro-filler (PET) and nano-filler (clay) are present at their higher ranges simultaneously in the nanocomposite system, the tensile strength decreases considerably. For example for nanocomposite constitutions (clay: 1.6875 wt. %, PET: 1.125 wt. %) and (clay: 2.25 wt. %, PET: 1.5 wt. %) where micro and nano-fillers both are present in a significant amount, the tensile strength dropped to lower values of 34.3 MPa and 27.6 MPa respectively. This shows that the epoxy-hardener system cannot accommodate both the fillers simultaneously in large amounts. This is because increasing the filler contents to higher concentrations, increases the viscosity of the system resulting in heterogeneity and nano voids formation due to entrapment of air bubbles during sample preparation (Azeez *et al.,* 2013).

Bending Strength

- The bending strength for the neat epoxy-hardener system has been observed to be 93.7 MPa. Addition of fillers (either clay, or PET or both) has lowered the bending strength with reference to that of the neat epoxy-hardener system.
- The maximum bending strength observed for the nanocomposite system (blend) is 83.3 MPa for 2.25 wt. % clay with no PET addition. For maximum clay loadings epoxy nanocomposites

showed maximum bending strength as compared to other blends. This was justified by the good interfacial bonding between the nanoclay filler and the epoxy matrix, which leads to increased surface area of matrix/nanoclay interaction and good stress transfer from the matrix to the nanoclay (Kusmono *et al.,* 2013).

- Further, it has been observed that, when both the fillers are present in the nanocomposite system and that too in their higher ranges, the bending strength values drop drastically. Thus, concluding that there is some upper limit of the total micro and nano filler content which the nanocomposite system can accommodate.
- Also, for the composite containing only PET fibers, bending strength has been observed to be low. It can be concluded that short fibers do not support the transverse load well, thus deteriorating the resistance against flexural loading.

Flexural Modulus

- The flexural modulus of neat epoxy-hardener system is 3196.7 MPa.
- Improvement in flexural modulus has been observed for the epoxy-clay blend containing maximum weight percentage of clay and has been about 10% over that of the base material. The reinforcing effect of clay layers on the flexural modulus is mainly due to the high modulus and high aspect ratio of the dispersed clay layers. This provides large interfacial interaction between clay layers and polymer matrix (Isik *et al.,* 2003; Azeez *et al.*, 2013; Kusmono *et al.*, 2013).
- With addition of only PET to the composite system, the flexural modulus decreased significantly. For example, for the composition (0 wt. % clay, and 1.5 wt. % PET), the flexural modulus was 2860 MPa. This is again attributed to the shorter length of micro-fillers in the composite system.
- The nanocomposites containing both PET and clay in their higher ranges, has deteriorated the flexural modulus considerably. This was due to increased secondary content which leads to decrease in flexural modulus values, which could be explained by the stress concentration sites. These sites form due to the higher content leading to lowering of filler surface area and lower polymer/clay surface interaction (Kusmono *et al.*, 2013).

Effect of Surface Modification on Nanocomposite Properties

- The treatment of fibers has been done to reduce their excessive smoothness and chemical inertness. Excessive smoothness reduces the extent of mechanical bonding and chemical inertness reduces the extent of chemical bonding between the fibers and the matrix.
- PET fibers have been treated under different temperature-time conditions. Three temperatures were chosen for the fiber treatment: room temperature (31 ℃), a temperature below the glass transition temperature of PET (50 ℃), and a temperature above the glasss transition temeprature of PET (80 ℃). For each temperature, PET fibers have been treated for atleast four different soaking periods viz. 2.5, 5.0, 10.0, 15.0 min respectively.
- For all the temperature-time treatment conditions at 31 ℃ and 50 ℃, no significant morphological changes on the surface of PET fibers have been observed. Similar results have been obtained for treatment at 80 ℃ for 2.5 and 5.0 min repectively. However, significant changes have been observed at the surface of PET fibers for prolonged treatment of 10 and 15 min at 80 ℃. But for excessively long treatment periods of 30 and 45 min respectively, the PET have lost their surface integrity due to development of large craters, excessive bending etc. This was in accordance with the work of Teh et al. (2005) which reports that soaking for prolongrd time periods results in aqueous alkali reacting with highly stressed ester bonds within the structure resulting in rapid hydrolysis.

Fig. 4.5 (a–d) shows the SEM images for the treatment temperature of 31 ℃ (room temperature) with treatment time periods of 2.5, 5, 10, 15 minutes respectively. The areas of modification by NaOH on the surface are seen like minute pores as seen in Fig. 4.5 (d). SEM images show that surface has not been modified adequately (not sufficiently rough) to provide any increased adhesion of PET to the resin.

5.3 Major Conclusions

- The results of the study reveal that it is possible to successfully fabricate nanocomposites with a low viscosity epoxy of araldite family (resin: GY 257, and hardener: HY 837) containing two fillers (micro as well as nano) to give moderate to good mechanical properties.
- The results of the study show that the presence of a silicate based filler (in the present study, clay was the silicate based nano-filler) and a thermoplastic based filler (PET was the

thermoplastic based micro-filler) have diverse effect on the mechanical properties of the nanocomposite system. The increase in silicate based nano-filler has more profound effect in giving favorable flexural properties whereas the increase in PET micro-filler has more significant effect on the tensile properties.

- The results of the experimental work have shown that the nanocomposite system is not able to accommodate the simultaneous presence of both the micro and nano-fillers in a significant amount.
- The present work also reveals that the alkaline treatment for PET fibers is effective in bringing favorable and significant morphological changes on the surface of treated fibers. This surface modification probably improvers both the mechanical and chemical adhesion between the fiber reinforcement and the matrix leading to improved tensile strength. In the present work, tensile strength improved considerably by fabricating nanocomposite with fibers treated under the selected conditions.

5.4 Scope of Future Work

The present work investigated the effect of micro and nano-filler concentration on the mechanical properties of a nanocomposite system. The main properties investigated were tensile and flexural. However, the presence of thermoplastic based ductile PET fibers have a great potential in improving the resistance against impact loading. The work can be extended to evaluate the impact strength of the nanocomposite system with changes in PET and clay loadings. Also, the given nanocomposite system contained clay as the silicate based nano-filler. The presence of clay can have a marked effect in improving the physical properties of the nanocomposite system. So, another scope can be to investigate the effect of clay concentration on the glass transition temperature, storage modulus and barrier properties etc.

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Appendix I

Peak list for Pristine Clay

Pos. [°2Th.]	**Height [cts]**	**d-spacing [Å]**	**Rel. Int. [%]**	**Area [cps*°2Th.]**	**Area [cts*°2Th.]**	**FWHM [°2Th.]**
4.4216	2992.11	**19.96835**	100.00	13.89	1154.47	0.2608
4.8024	2778.26	18.38574	92.85	12.90	1071.96	0.2608
19.7527	1748.97	4.49095	58.45	6.49	539.86	0.2086
21.9606	601.27	4.04417	20.10	2.23	185.59	0.2086
24.6891	349.13	3.60307	11.67	4.54	377.19	0.7301
26.5999	260.74	3.34842	8.71	0.97	80.48	0.2086
34.7530	554.31	2.57928	18.53	3.09	256.65	0.3129
36.2404	440.84	2.47675	14.73	6.55	544.30	0.8344
40.2849	57.49	2.23693	1.92	0.64	53.23	0.6258
53.9025	223.76	1.69957	7.48	2.49	207.21	0.6258
61.7837	712.73	1.50033	23.82	5.29	440.00	0.4172
72.9098	175.78	1.29639	5.87	1.96	162.77	0.6258
76.3017	146.99	1.24698	4.91	2.25	186.97	0.6360

Peak list for composite with 0.75 wt. % clay

Pos. [°2Th.]	**Height [cts]**	**d-spacing [Å]**	**Rel. Int. [%]**	**Area [cps*°2Th.]**	**Area [cts*°2Th.]**	**FWHM [°2Th.]**
3.0059	325.73	**29.36900**	100.00	2.66	248.60	0.3816

Peak list for composite with 1.5 wt. % clay

Pos. [°2Th.]	**Height [cts]**	**d-spacing [Å]**	**Rel. Int. [%]**	**Area [cps*°2Th.]**	**Area [cts*°2Th.]**	**FWHM [°2Th.]**
2.9384	485.75	**30.04329**	21.50	1.61	149.94	0.2086
5.8675	170.44	15.05042	7.55	0.85	78.92	0.3129
19.6959	2258.78	4.50377	100.00	22.41	2091.67	0.6258

Peak list for composite with 2.25 wt. % clay

Pos. [°2Th.]	**Height [cts]**	**d-spacing [Å]**	**Rel. Int. [%]**	**Area [cps*°2Th.]**	**Area [cts*°2Th.]**	**FWHM [°2Th.]**
2.9894	937.31	**29.53061**	100.00	5.42	506.31	0.3651
6.0058	284.96	14.70407	30.40	1.88	175.92	0.4172
61.7440	80.93	1.50120	8.63	1.32	123.53	0.7632

Peak list for composite with 3 wt. % clay

Pos. [°2Th.]	**Height [cts]**	**d-spacing [Å]**	**Rel. Int. [%]**	**Area [cps*°2Th.]**	**Area [cts*°2Th.]**	**FWHM [°2Th.]**
3.0221	797.66	**29.21111**	100.00	3.96	369.32	0.3129
6.1876	191.71	14.27250	24.03	0.95	88.76	0.3129
61.6269	109.85	1.50377	13.77	1.20	111.78	0.5088

Appendix II

Estimated Regression Coefficients for Tensile Strength (MPa)

Terms	Coef	P
Epoxy-Hardener system (%)	38	*
Clay (%)	5296036	*
PET (%)	-5852655	*
Epoxy-Hardener system (%)*Clay (%)	-6768329	0.571
Epoxy-Hardener system (%)*PET (%)	5942170	0.696
Epoxy-Hardener system (%)*Clay (%) *PET (%)	1912684	0.783

R-Sq = 88.04% R-Sq(pred) = 71.06% **R-Sq(adj) = 81.51%**

Analysis of Variance for Tensile Strength (MPa)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	6	372.800	372.8002	62.1334	13.49	0.000
Linear	2	236.477	16.3657	8.1828	1.78	0.214
Quadratic	2	119.528	16.3983	8.1991	1.78	0.214
Epoxy-Hardener*Clay (%)	1	77.150	1.5705	1.5705	0.34	0.571
Epoxy-Hardener*PET (%)	1	42.379	0.7388	0.7388	0.16	0.696
Special Cubic	1	13.677	0.3672	0.3672	0.08	0.783
Epoxy-Hardener*Clay (%)*PET (%)	1	13.677	0.3672	0.3672	0.08	0.783
Full Cubic	1	3.118	3.1181	3.1181	0.68	0.428
Epoxy-Hardener*Clay (%)*(-)	1	3.118	3.1181	3.1181	0.68	0.428
Residual Error	11	50.653	50.6527	4.6048		
Total	17	423.453				

Appendix III

Estimated Regression Coefficients for Bending Strength (MPa)

Term	Coef	P
Epoxy-Hardener system (%)	95	*
Clay (%)	67530851	*
PET (%)	-104091598	*
Epoxy-Hardener system (%)*Clay (%)	-79553486	0.001
Epoxy-Hardener system (%)*PET (%)	105674839	0.001
Epoxy-Hardener system (%)*Clay (%)*PET (%)	48978290	0.001
Epoxy-Hardener system (%)*Clay (%)*(-)	10961061	0.002

R-Sq = 96.18% R-Sq(pred) = 90.95% **R-Sq(adj) = 94.09%**

Analysis of Variance for Bending Strength (MPa)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	6	3015.35	3015.35	502.558	46.14	0.000
Linear	2	1927.30	255.15	127.577	11.71	0.002
Quadratic	2	831.89	256.22	128.110	11.76	0.002
Epoxy-Hardener*Clay (%)	1	381.44	216.97	216.972	19.92	0.001
Epoxy-Hardener*PET (%)	1	450.45	233.64	233.644	21.45	0.001
Special Cubic	1	68.79	240.75	240.753	22.10	0.001
Epoxy-Hardener*Clay (%)*PET (%)	1	68.79	240.75	240.753	22.10	0.001
Full Cubic	1	187.36	187.36	187.360	17.20	0.002
Epoxy-Hardener*Clay (%)*(-)	1	187.36	187.36	187.360	17.20	0.002
Residual Error	11	119.81	119.81	10.892		0.001
Total	17	3135.16				

Appendix IV

Estimated Regression Coefficients for Flexural Modulus (MPa)

Term	Coef	P
Epoxy-Hardener system (%)	3261	*
Clay (%)	1894920369	*
PET (%)	-3088485853	*
Epoxy-Hardener system (%)*Clay (%)	-2194972289	0.000
Epoxy-Hardener system (%)*PET (%)	3135492885	0.000
Epoxy-Hardener system (%)*Clay (%)*PET (%)	1510299332	0.000
Epoxy-Hardener system (%)*Clay (%)*(-)	268534284	0.001

R-Sq = 96.38% R-Sq(pred) = 91.33% **R-Sq(adj) = 94.41%**

Analysis of Variance for Flexural Modulus (MPa)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	6	1573921	1573921	262320	48.83	0.000
Linear	2	697931	402277	201138	37.44	0.000
Quadratic	2	472890	404218	202109	37.62	0.000
Epoxy-Hardener*Clay (%)	1	637	165174	165174	30.74	0.000
Epoxy-Hardener*PET (%)	1	472254	205695	205695	38.29	0.000
Special Cubic	1	290646	228923	228923	42.61	0.000
Epoxy-Hardener*Clay (%)*PET (%)	1	290646	228923	228923	42.61	0.000
Full Cubic	1	112453	112453	112453	20.93	0.001
Epoxy-Hardener*Clay (%)*(-)	1	112453	112453	112453	20.93	0.001
Residual Error	11	59097	59097	5372	5.69	0.025
Lack-of-Fit	2	32994	32994	16497		
Pure Error	9	26104	26104	2900		
Total	17	1633018				